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Investigation of the electronic and thermal rearrangement properties of SPIRO[2,4]HEPTA-4,6-DIENES

Raymond K. Crandall

INVESTIGATION OF THE ELECTRONIC AND THERMAL REARRANGEMENT PROPERTIES OF SPIRO[2,4]HEPTA-4,6-DIENES

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THESIS

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APPROVED:

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ABSTRACT

The mechansism of thermally induced hydrogen and alkyl migrations in suitably substituted cyclopentadienes have been extensively studied. Although the course and mechanism of alkyl shifts in cyclopentadienes have been investigated, there is currently a lack of agreement on the precise mechanisms of alkyl migrations. It is apparent that the mechanism is largely dependent on the nature of both the migrating substituent and upon other substituents in the molecule and, in some cases, the shift may occur by more than one competing mechanism. Alkyl shifts in spiro substituted cyclopentadienes have been clearly shown to proceed *via* a concerted pathway. However, the participation of a biradical process has not been excluded.

The purpose of this research was to clarify the exact nature of the alkyl shift in appropriately substituted spiro[2.4]hepta-4,6-dienes as to concerted or biradical. Previous work has shown that 4-methylspiro[2.4]hepta-4,6-diene rearranged to an equilibrium mixture of approximately equal amounts of 4 and 5-methylspiro[2.4]hepta-4,6-dienes. The slightly positive entropy of activation of the dual alkyl migration as well as other previous similar work suggested a possible biradical component to the rearrangement. The effects of ring strain in the intermediate as well as stabilization resulting from alkyl substitution were of particular interest. The appropriate molecule for study of the rearrangement would have a geometric label on the five membered ring to detect alkyl migration and a stereochemical label on the three membered ring to detect biradical formation during the rearrangement.

The *cis*-2,3,4-trimethylspiro[2.4]hepta-4,6-diene molecule was prepared by photolysis of the methyldiazocyclopentadiene in *cis*-2-butene solution and purified by gas liquid chromatography. The static pyrolysis results showed that the products of the approximate first order thermal rearrangements were consistent with a biradical pathway. The products derived from the equilibrium mixture gave no evidence for a significant concerted mechanism operating. It is impossible to exclude the simultaneous operation of a slower concerted pathway with the results of this research.

AKNOWLEDGEMENTS

A special word of thanks goes to my research advisor, Dr. Robert Clark, for his unlimited patience and understanding through many long hours of discussion and counseling which guided me to this conclusion. This cooperative spirit was present in the entire research group, resulting in support and helpful suggestions from Dave Youngs, Jim Mondo, and George Frade.

The author is deeply thankful for the support given by the Rochester Institute of Technology throughout this effort. The members of the faculty were always supportive. The work would not have been possible without the financial aid given in the form of teaching assistantships and stipends. The quality of the program is maintained at high levels and certainly will be a substantial aid to future career goals.

The support of my family, in particular, my wife, Casey, has been indispensible to the completion of this work. Her dedication to many efforts at typing this manuscript, including the present copy, has been admirable. A number of other people have been extremely helpful. Nancy Karner of Xerox Corporation spent many hours reviewing the text for language usage and made many helpful suggestions. Jean Taber of Xerox supplied technical expertise necessary to create the molecular diagrams in the text and figures. Bob Sperry of Xerox has been extremely helpful in many technical consultations on usage of the Alto System for this manuscript. The author is also grateful to Xerox for use of the highly sophisticated Alto System and Laser Printers.

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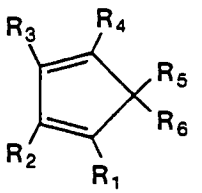
The mechanisms of thermally induced hydrogen and alkyl migrations in suitably substituted cyclopentadienes, 1 have been extensively studied[1-5]. Although the course and mechanism

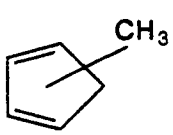


1

of alkyl shifts in cyclopentadienes have been investigated, there is currently a lack of agreement on the precise mechanism of alkyl migrations[6]. It is apparent that the mechanism of the alkyl shift is largely dependent on the nature of both the migrating substituent and upon other substituents in the molecule, and, in some cases the shift may occur by more than one competing mechanism[7].

1B. Hydrogen Shifts in Alkyl Cyclopentadienes.

Hydrogen shifts in the monomethyl-, dimethyl-, trimethyl-, and tetramethylcyclopentadienes 2, 3, 4 and 5 were first reported in 1963[8] to proceed under relatively mild conditions to provide an equilibrium mixture of positional isomers.



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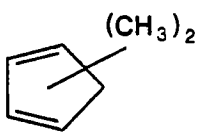

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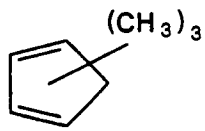

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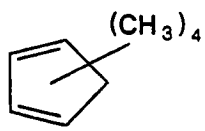

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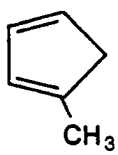
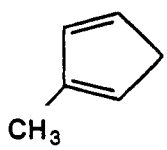
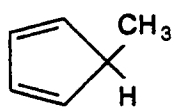
Methylcyclopentadiene (2a-c) is obtained from most preparations as a mixture of positional isomers[9]; predominantly 1-methyl-cyclopentadiene (2a) and 2-methylcyclopentadiene (2b) in



2a



2b



2c

approximately a one-to-one ratio, plus a trace of 5-methylcyclopentadiene (2c). A sample of pure 2a or pure 2b will rearrange at room temperature in one or two days by a sequence of hydrogen migrations to provide the equilibrium mixture. McLean and Haynes[10,11] later substantiated the rearrangements of 2,3,4 and 5 resulting from hydrogen migrations and investigated the kinetics of these rearrangements. The equilibrium mixture 2a:2b:2c was more accurately determined to be 45:54:1. The activation energy for the kinetically first-order process was 20.4 kcal/mole and the entropy of activation -10 e.u. over a temperature range of 278°K to 313°K. Mironov[8] explained the facility of the hydrogen shifts in 2,3,4 and 5 in terms of a migrating proton around the periphery of the cyclopentadienide ion (Figure 1) which has the stabilized Huckel aromatic configuration of 6 *pi* electrons.

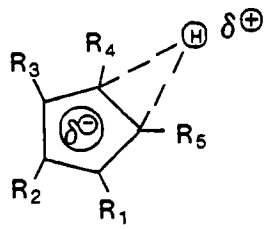


Figure 1. Hydrogen shift in alkylcylopentadienes

Certainly this is one plausible explanation for the hydrogen shift. McLean and Haynes [10,11] noted that, in the presence of hydroxide or sodium cyclopentadienide, 2a rearranges so rapidly that kinetic measurements were not possible. In the solution phase under basic conditions, hydrogen shifts of alkylcyclopentadienes would be expected to proceed ionically due to relatively high Bronsted acidity ($K_a = 10^{-15}$) of cyclopentadiene[12]. However, the mechanism of the thermally induced unimolecular hydrogen shift in the gas phase is probably more appropriately rationalized by the polarized transition state shown in Figure 1.

The intramolecular thermal hydrogen shift in alkylcyclopentadienes, reported as 1,2 shifts by both Mironov[3,8] and McLean and Haynes[10,11], is now well known. The hydrogen shift is mechanistically more correctly designated as a [1,5] shift. The rules of Woodward and Hoffman[13] require the conservation of orbital symmetry in thermally induced concerted migrations in pentadienes as depicted in Figure 2.

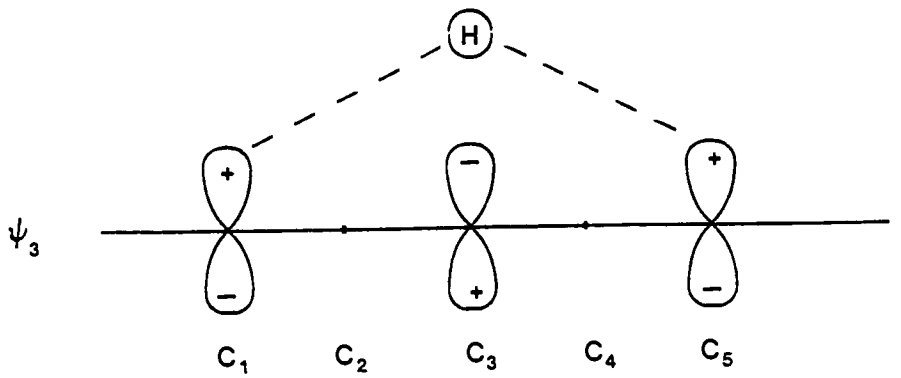


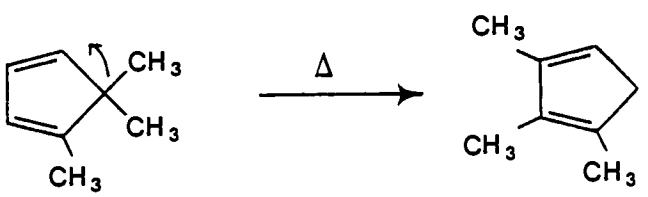
Figure 2. Orbital symmetry conservation of thermal [1,5] hydrogen shifts in 1,3-pentadiene

The mixing orbitals must be of the same symmetry in order for the orbital overlap to be bonding in the transition state for concerted migration. The highest occupied molecular orbital (HOMO) shown in Figure 2 is the pentadiene orbital which controls the stereochemistry of migration in concerted thermal shifts in 1,3- pentadienes. In order to maintain mixing of orbitals, the migrating system must traverse the same face of the conjugated system (i.e., suprafacial) in the migration from C_1 to C_5 as shown in Figure 2. The designation of [1,5]-sigmatropic shifts applies to concerted alkyl migrations in pentadienes as well.

1C. Thermally Induced Alkyl Shifts in Cyclopentadienes.

Alkyl [1,5] shifts in cyclopentadienes were first reported by Kloosterziel and de Haan[14]. The 1,5,5-trimethylcyclopentadiene (**6a**) rearranges thermally to exclusively provide 1,2,3-trimethylcyclopentadiene (**6b**) (Scheme 1).

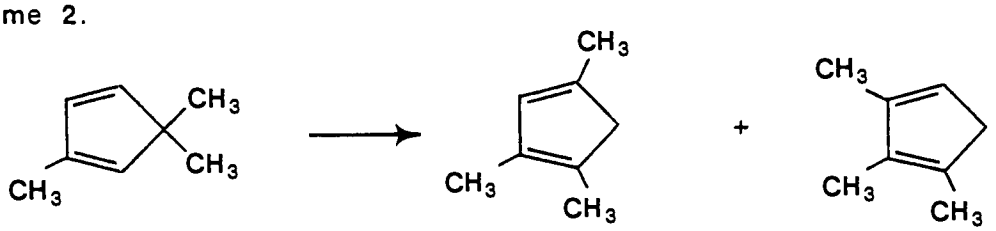
Scheme 1.



6a **6b**

The 2,5,5-trimethylcyclopentadiene (**6c**) rearranges at a rate five times that of **6a** to two isomers; 1,2,4- and 1,2,3- trimethylcyclopentadiene, (**6d,6b**) (Scheme 2).

Scheme 2.

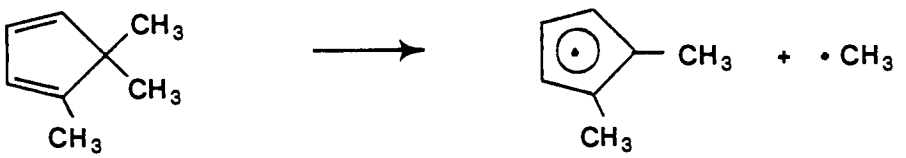


6c 6d 6b

The rearrangement was said to proceed *via* an intramolecular concerted process involving the sigmatropic [1,5] alkyl shift of a methyl group followed by a [1,5] hydrogen shift. The possible radical chain mechanism[6] in Scheme 3 was eliminated by noting that the presence

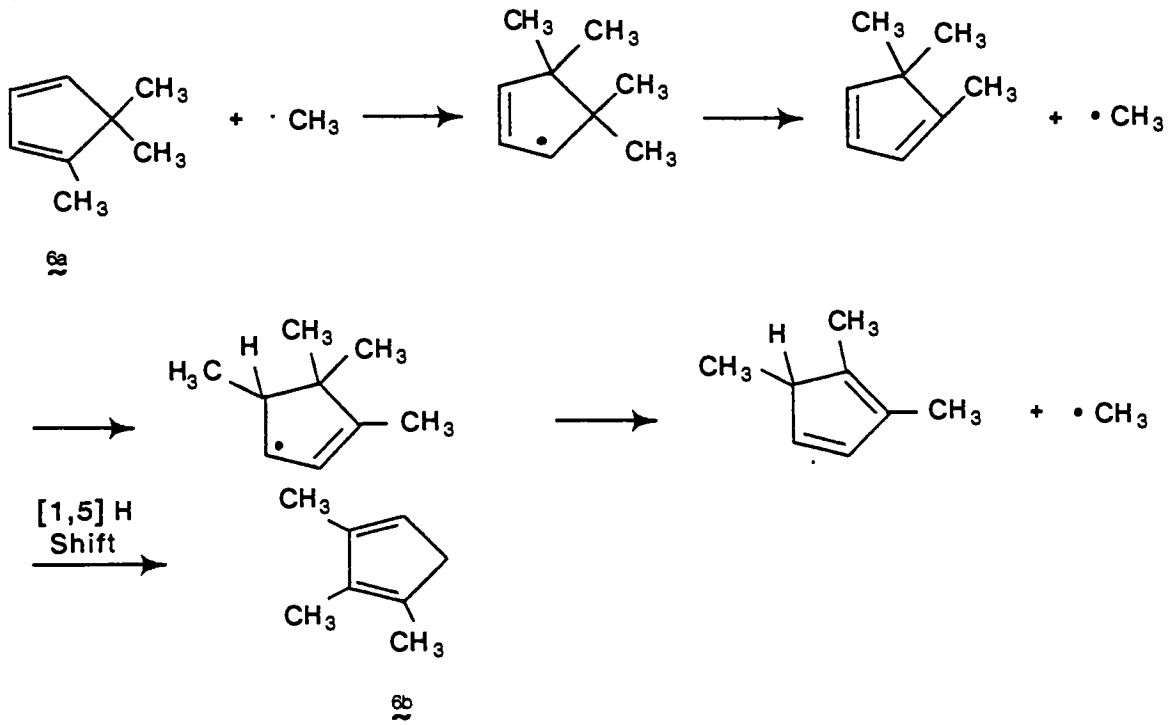
Scheme 3

Initiation



6a

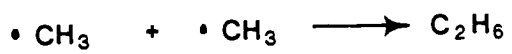
Propagation



6a

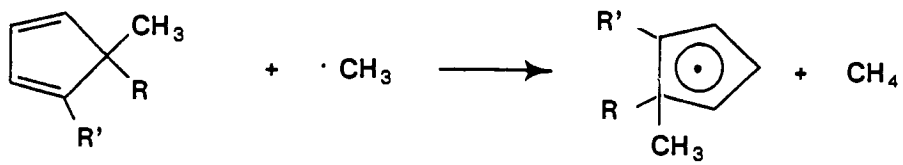
6b

Termination



of di-*tert*-butylperoxide. a radical source, in the gas phase pyrolysis reactor had no effect on the reaction rate. Similarly, the addition of a radical scavenger, propene, had no effect on the reaction. It was further noted that derivatives of 6a and 6c with abstractable hydrogen atoms would form during the progress of the pyrolysis. It was postulated these would be expected to react with any methyl radical present to yield a stabilized cyclopentadienyl radical (Scheme 4) and hence terminate the chain.

Scheme 4.

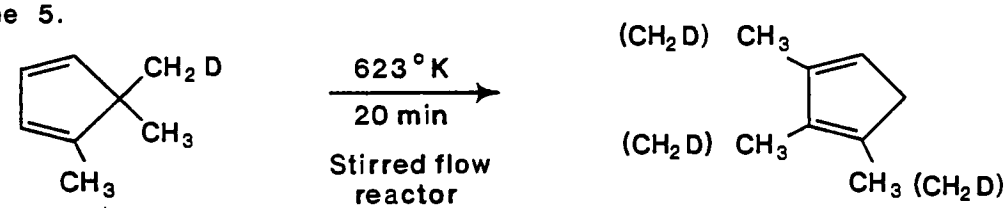


Since the rearrangement followed first order kinetics, and no inhibition was noted, the radical chain mechanism was discarded from further consideration.

A radical dissociation-recombination reaction was also dismissed by pointing out the unlikely probability of a cage effect in the gas phase and, more importantly, the absence of the 1,2,4-trimethyl isomer (6a), which had been shown to yield exclusively 1,2,3-trimethylcyclopentadiene (**6b**). It seemed unreasonable to the researchers that a radical pair could reassociate to exclusively **6b** and not 6d. The mechanism proposed is a sigmatropic [1,5]-methyl shift analogous to the [1,5] hydrogen shift (see above).

Willcott and Rathburn[6] have cited an example of an intermolecular methyl shift in 1,5,5-trimethycyclopentadiene (6a), in which one of the methyl groups is tagged with one deuterium atom (Scheme 5).

Scheme 5.



7 8

The reactant **7** is present at a pressure of 10 mm in approximately one atmosphere of nitrogen. The deuterium content of reactants and products as determined by Willcott and Rathburn[6] by mass spectrometric analysis is summarized in Table 1.

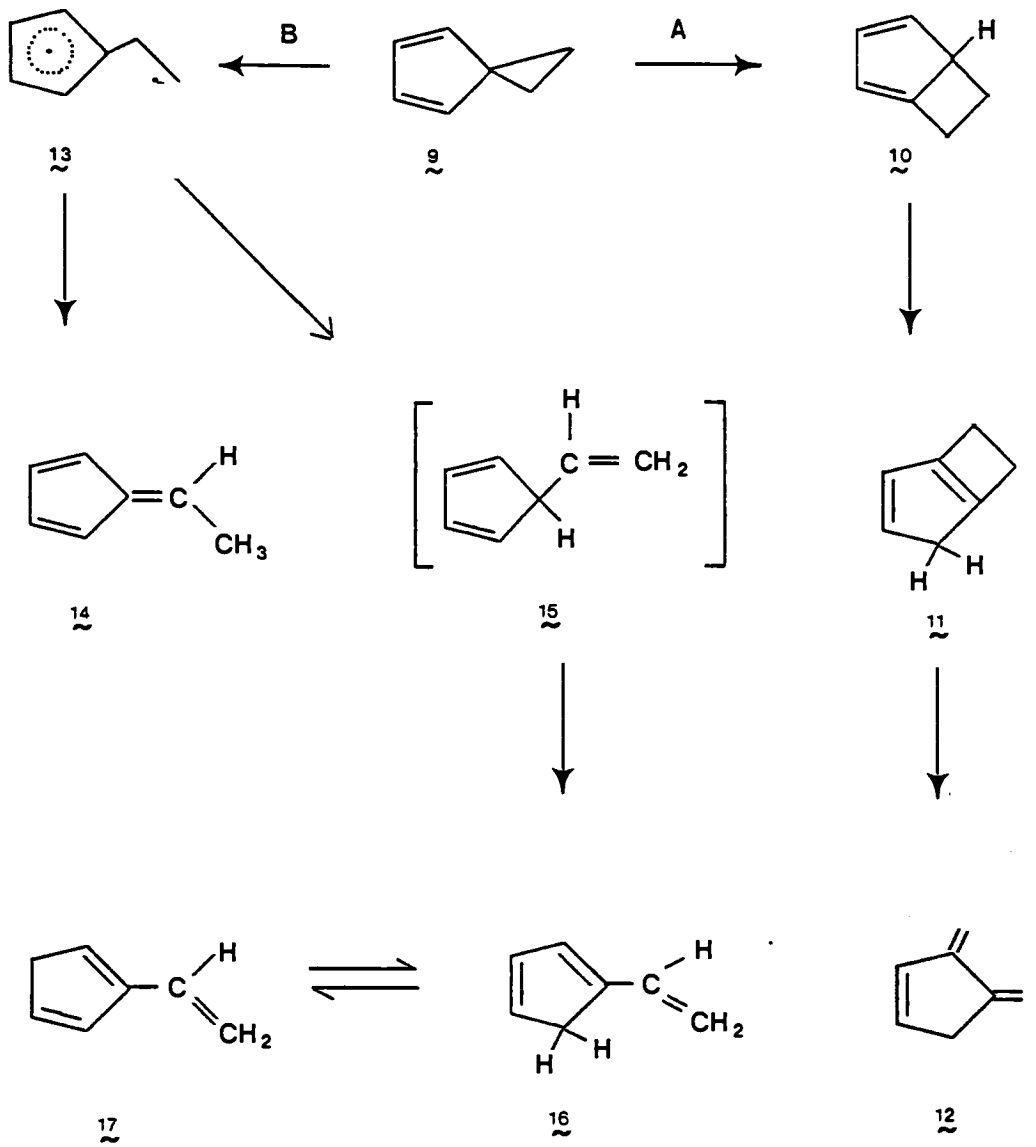
Table 1. Deuterium Distribution in a Monodeuterium Labeled Methyl Group in 1,5,5-Trimethylcyclopentadiene (7).

Deuterium Content	%7	%8
d_0	5.4	23.0
d_1	90.5	60.0
d_2	3.7	15.0
d_3	0.4	2.0

The isotopic distribution demonstrates that 90.5% of the starting material 7 contains one deuterium atom per molecule. The product 8 shows a redistribution of deuterium with an increase in the non-deuterated (d_0), di- and tri-deuterated species. The authors proposed the radical chain mechanism shown in Scheme 3 (see above) to be in operation. Calculations show that a rearrangement proceeding exclusively *via* the radical chain mechanism would yield a deuterium isotopic distribution in 8 of 50 percent d_1, and 25 percent d_0 and d_2. The discrepancy between the predicted and experimental distribution of deuterium was considered to be more likely due to a significant degree of simultaneous operation of the concerted pathway, rather than a kinetic isotope effect of inordinate magnitude. The exclusive preference for 1,2,3-trimethylcyclopentadiene (6b) was rationalized by the stability of the allylic radical involved in its formation (Scheme 3). It was concluded that thermally induced alkyl shifts in alkyl cyclopentadienes seem to demonstrate a delicate energy balance between the radical pathway (estimated E_A = 50 - 56 kcal/mole) and the concerted pathway (E_A = 42 kcal/mole).

Krekels, Dane, de Haan and Kloosterziel[15,16] first pyrolyzed spiro[2.4]hepta-4,6-diene (9). This ring system is particularly useful in the study of 5,5-disubstituted cyclopentadienes since the reaction is now restricted solely to an intramolecular process. The reaction (Scheme 6) was followed closely over a temperature range of 618°K to 673°K in a micro flow reactor, under nitrogen flow, by gas-liquid chromatography (capillary columns).

Scheme 6



Note that Pathway A in Scheme 6 is proposed to proceed *via* the bicyclo[3.2.0]hepta-1,3-diene (**10**) intermediate and presumably represented concerted migration of a cyclopropyl methylene fragment followed by a [1,5] hydrogen shift and electrocyclic ring opening to yield 3,4-dimethylenecyclopentene (**12**); Pathway B proceeds *via* the diradical **13**, and yields 6-methylfulvene (**14**) and the isomeric vinylcyclopentadienes (**16** and **17**). The product distribution ratio of **14** : **16** : **17** (0.49 : 0.40 : 0.11), was temperature independent. The distribution ratio of (**14** + **16** + **17**) : **12** varied with temperature, favoring **14** + **16** + **17** with increasing temperature. The kinetic determinations showed first order decay of the spirodiene **9**, as shown in Table 2.

Table 2 Activation Parameters in Pyrolysis of Spiro[2.4]hepta-4,6-diene (9).

Pathway[a]	Log A	E_A(kcal/mole)	$\Delta S^{\ddagger}$(cal/^{o}.mole)	$\Delta H^{\ddagger}$(kcal/mole)
A	10.98	38.1	-15	36.8
B	13.84	47.1	+3	45.8

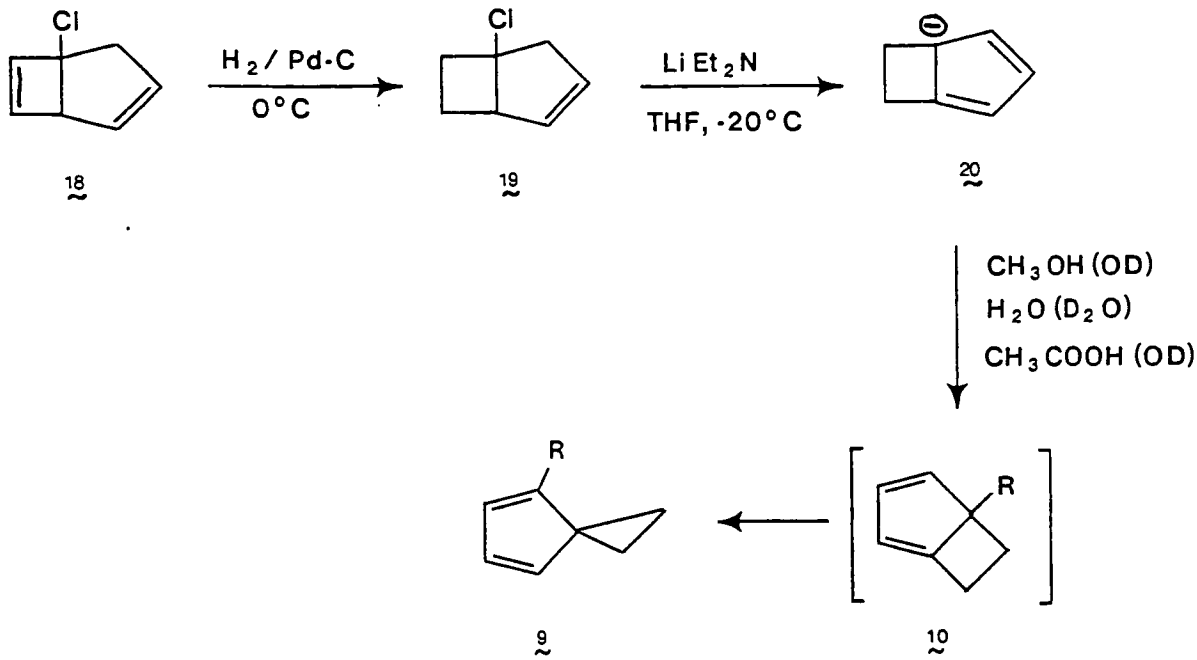
a. pathway A and B are depicted in Scheme 6.

The thermochemistry of small ring compounds, particularly cyclopropane, becomes significant here. The pyrolysis of cyclopropane yielding propene occurs at an appreciable rate only at temperatures greater than 773^{o}K[18]. The pyrolysis of 1,1-dimethylcyclopropane occurs at similar temperatures and is non-selective giving a statistical distribution of 3-methyl-1-butene and 3-methyl-2-butene. However, geometric isomerisation of the *cis*-labeled 1,2-dideuterio-1,2-dimethylcyclopropane occurs at conditions significantly milder than those required for ring opening (E_A = 65 kcal/mole and log A = 15). Breslow[17] has stated that the rate determining step must involve hydrogen migration as well as formation of trimethylene diradical. The magnitude of the Arrhenius pre-exponential factor agrees well with the proposed intermediate diradical, which would be preceded by a loose transition state on the energy surface. It is clear that the geometric isomerisations of cyclopropanes occur prior to formation of ring opening products, and most likely involve a diradical intermediate.

The thermal rearrangement of spiro[2.4]hepta-4,6-diene (**9**), in comparison to alkyl cyclopentadienes is complicated by cyclopropane thermochemistry. The energetics of bond homolysis and concerted migration, must be considered as well as relief of ring strain after bond breakage, and the ring strain in the concerted pathway to the bicyclo[3.2.0]heptadiene intermediate (**10**). (Note that in **10** the rings are locked together in approximate coplanarity; in spirodiene **9**, the plane of the cyclopropane ring bisects the plane of the cyclopentadiene ring in a perpendicular fashion). Presumably, the more nearly coplanar configuration of **10** is more severely strained than the spiro configuration of spirodiene **9**.

Oda and Breslow[19] reported the attempted synthesis of bicyclo[3.2.0]hepta-1,3-diene (10) but observed that it could not be isolated, even at -50°C (223°K). The synthetic route involved partial hydrogenation of the related chlorodiene (18) over palladium-carbon catalyst in pentane at 0°C (273°K) to give the chlorobicyclo[3.2.0]heptene (19) (Scheme 7) which

Scheme 7.

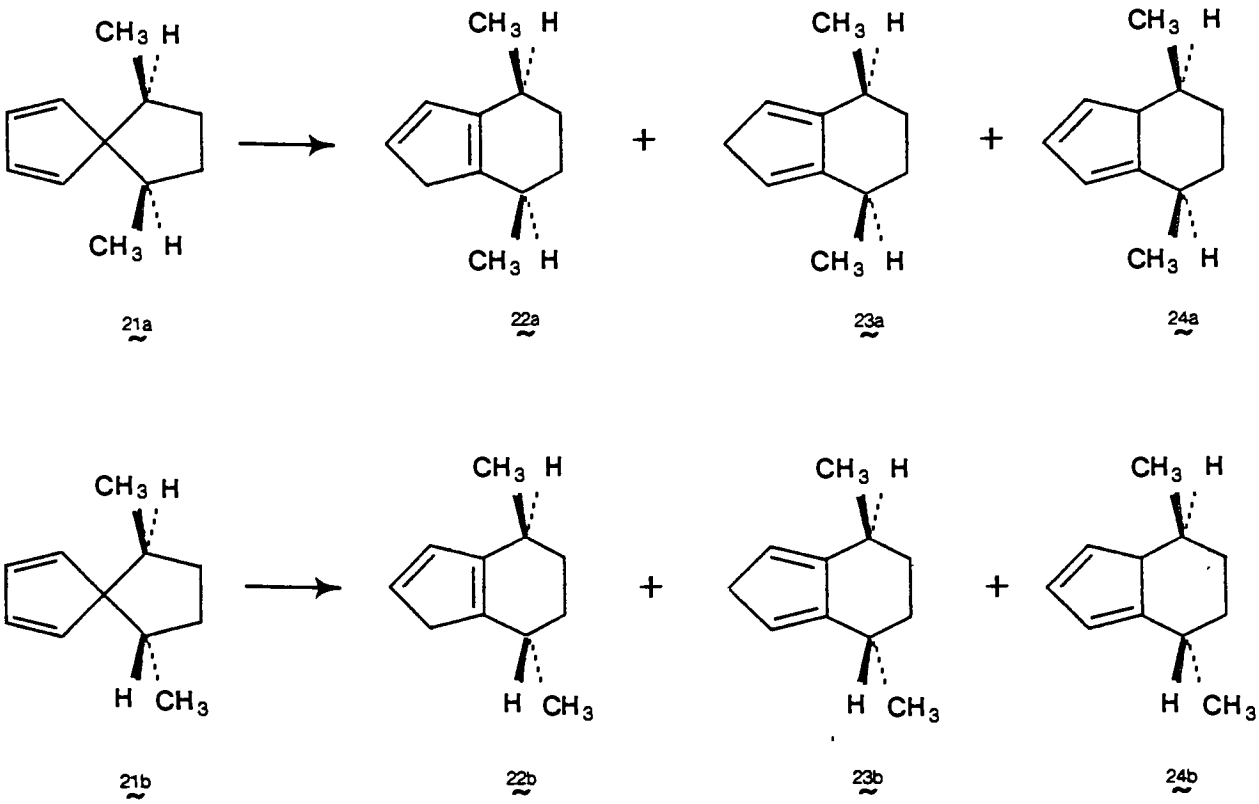


18 19 20 9 10

was subsequently dehydrochlorinated in tetrahydrofuran at -20°C (253°K) with lithium diethylamide to yield the bicyclic anion 20. Protonation, deuteration or methylation of the anion by methanol, water, acetic acid, their deuterated analogs or methyl iodide, respectively, led to spirodiene 9 as the only distillable product. Although 10 was probably formed *via* protonation, deuteration or methylation, the alkyl migration through ring contraction to spirodiene 9 was suggested to occur before hydrogen migration in 10. The preference of alkyl migration (E_A = 40 kcal/mole in related monocylic cyclopentadiene systems) to hydrogen migration (E_A = 20 kcal/mole) clearly establishes the instability of the coplanar configuration of 10.

The intervention of the concerted pathway in thermal rearrangements of certain spirocyclopentadienes has been clearly established by Boersma, de Haan, Kloosterziel and van de Ven[20]. Over a temperature range of 503°K to 553°K *cis*-6,9-dimethylspiro[4.4]nona-1,3-diene (21a) was pyrolysed in a micro flow reactor. The reactions were completely stereospecific (Scheme 8), with the *cis*-dimethyl labeled spirodiene 21a yielding exclusively the *cis*-dimethyl labeled bicyclic products 22a, 23a & 24a. Similarly, *trans* spirodiene 21b

Scheme 8.

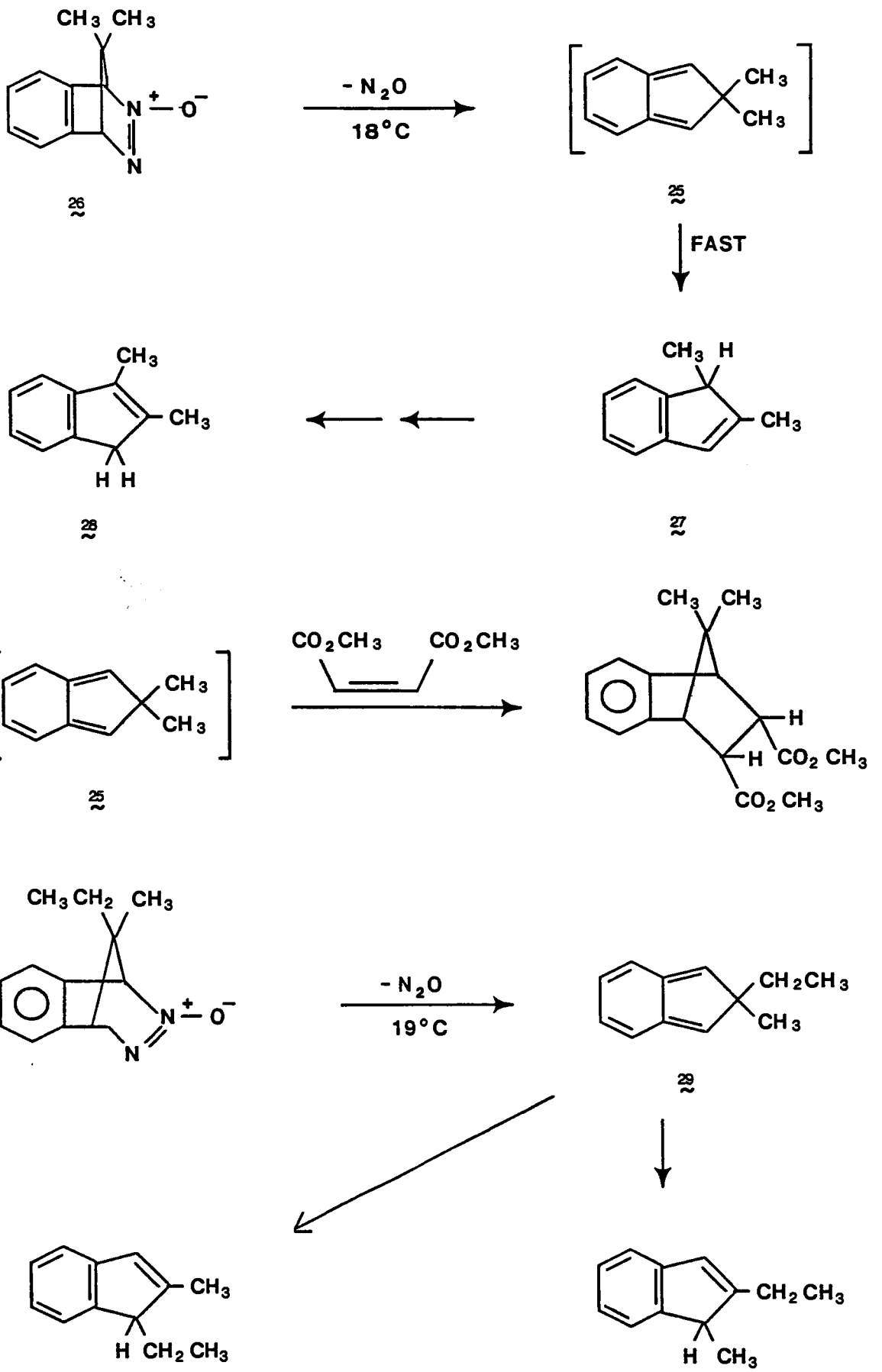


gave exclusively *trans* bicyclic products. **22b**, **23b** and **24b**. The *cis* and *trans* methyl labeled spiro[4.5]deca-1,3-dienes also showed complete stereospecificity in the analogous thermal rearrangement.

These rearrangements were shown to follow first order kinetics at an activation energy of 35.6 kcal/mole for the spiro[4.4]diene **21** and 46.7 kcal/mole for the spiro[4.5]diene. The results are in agreement with the predictions of orbital symmetry conservation for [1,5] sigmatropic carbon migrations. It was therefore concluded that the [1,5] alkyl shifts are concerted sigmatropic, suprafacial shifts demonstrating retention of configuration of the migrating carbon, in accord with the rules of Woodward and Hoffmann. The subsequent [1,5] hydrogen shift was assumed to be of sufficiently low activation energy in comparison to the alkyl shift such that it is not involved in the rate determining step. The exclusive preference of the rearrangement for the concerted pathway as opposed to the diradical is presumably due to the absence of any significant energetically unfavorable ring strain effects in these bicyclic products, **22**, **23** and **24** as compared to the bicyclo[3.2.0]heptadiene (**10**), which would be partially reflected in the transition state for concerted migration.

Dolbier, McCullagh, Rolinson and Annapole[21] have reported a concerted migration of a methyl group in the transient 2,2-dimethyl-2H-indene (**25**) obtained from the azoxy species **26** (0.05M solution of **26** in benzene at 180°C (453°K) extrudes nitrous oxide; Scheme 9).

Scheme 9.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- N2O
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H H
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CO2CH3
CO2CH3
CH3
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25
CH3 CH3
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H
CO2 CH3
CO2 CH3
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CH2 CH3
H CH3

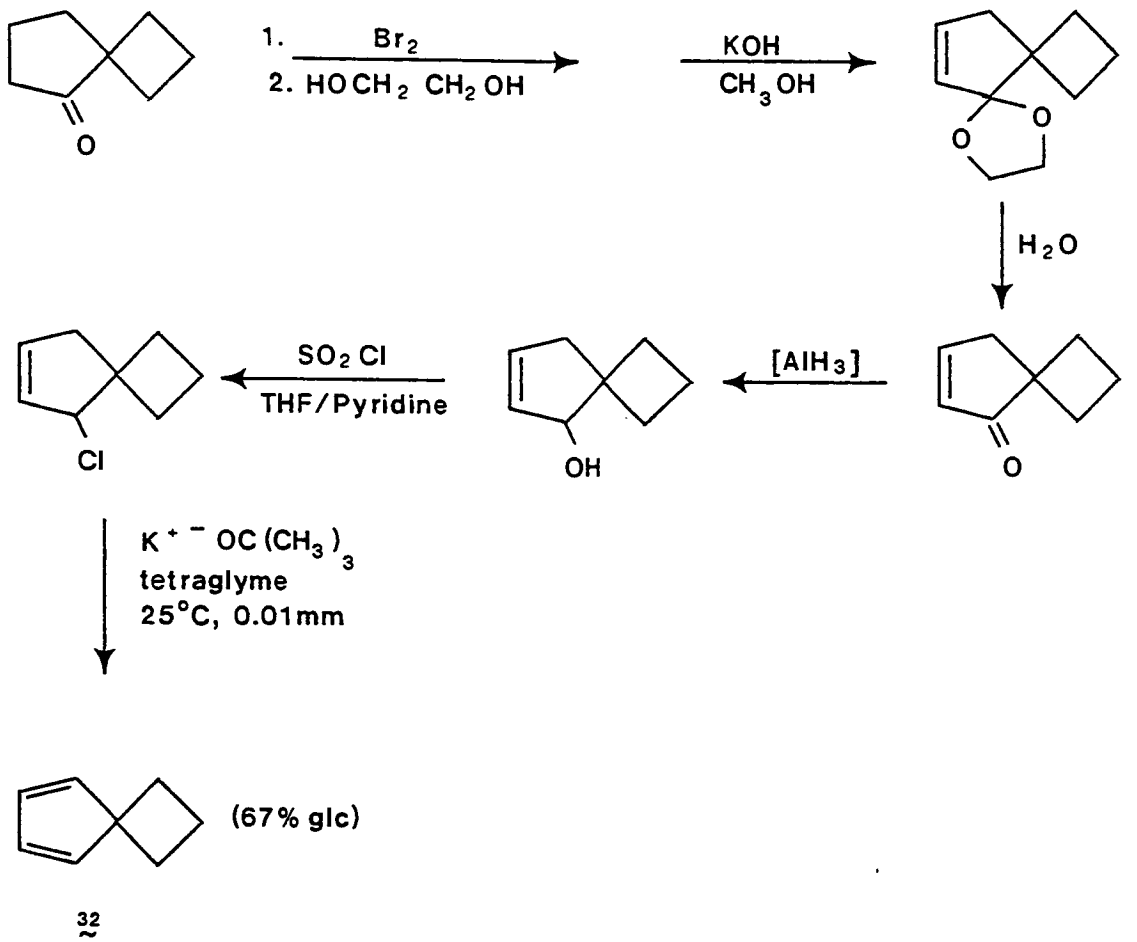
The presence of **25** as an intermediate in the process was clearly established by trapping with dimethyl maleate to form the corresponding Diels - Alder adduct (Scheme 9). The 2.2-dimethylisoindene **25** rearranged readily under the conditions of its synthesis to 1.2-dimethylindene (**27**) which subsequently rearranged at a slower undetermined rate to 2.3-dimethylindene (**28**). Kinetic determinations of the rearrangement of **26** and **27** were not possible because the process of nitrous oxide extrusion was involved in the rate expression.

A free radical chain mechanism for the [1.5] methyl shift was discounted because no decrease in yield was noted when cumene was used as the solvent, although the possibility of a rapid radical dissociation reassociation coupling mechanism in a solvent cage was not discussed. Further, a crossover experiment substituting one methyl substituent by an ethyl substituent in the azoxy species **26** gave 2-ethyl-2-methylindene (**29**) which rearranged exclusively to a mixture of 2-methyl-3-ethylindene (**30**) and 2-ethyl-3-methylindene (**31**). with less than 0.2% crossover products.

The synthesis[22,23] and thermal rearrangement[22] of spiro[3.4]octa-**5,7**-diene (**32**) has been reported. At 673°K in a flow pyrolysis system, the ratio of products **34**: **35** was 1: 0.8 (Scheme 10).

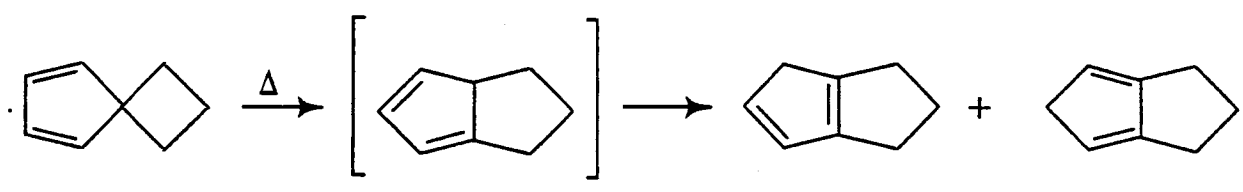
Scheme 10.

SYNTHESIS



32

THERMAL REARRANGEMENT

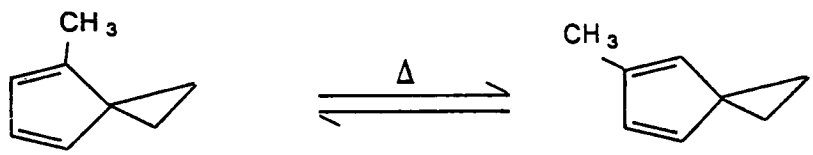


32 33 34 35

It was presumed that 33 is the initial species formed as a result of [1,5] alkyl migration, followed by [1,5] hydrogen shift. The activation enthalpy of the rearrangement was estimated at 28 kcal/mole. It was noted that the thermal rearrangement of the spiro[3.4]diene 32 is unlike that of the spiro[2.4]diene 9 and similar to that of spiro[4.4]diene 21. In comparison to 21, the rearrangement of 32 should proceed with greater facility, due to overall release of 20.2 kcal/mole ring strain energy when cyclobutane (ring strain of 26.7 kcal/mole) expands to cyclopentane (ring strain of 6.5 kcal/mole)[24]. This proposal is in qualitative agreement with the estimated activation enthalpy. However, the precise mechanism(s) of the thermal rearrangement of 32 cannot be established without further work, such as labeling the cyclobutane ring and determining the stereospecificity, or lack thereof, of the rearrangement.

The synthesis and thermal rearrangements of 4- and 5- methylspiro[2.4]hepta-4,6-diene (36,37) were reported by this group[25]. The unusual aspects of the rearrangement (Scheme 11) is the retention of the cyclopropane ring in the thermally rearranged product.

Scheme 11



36 37

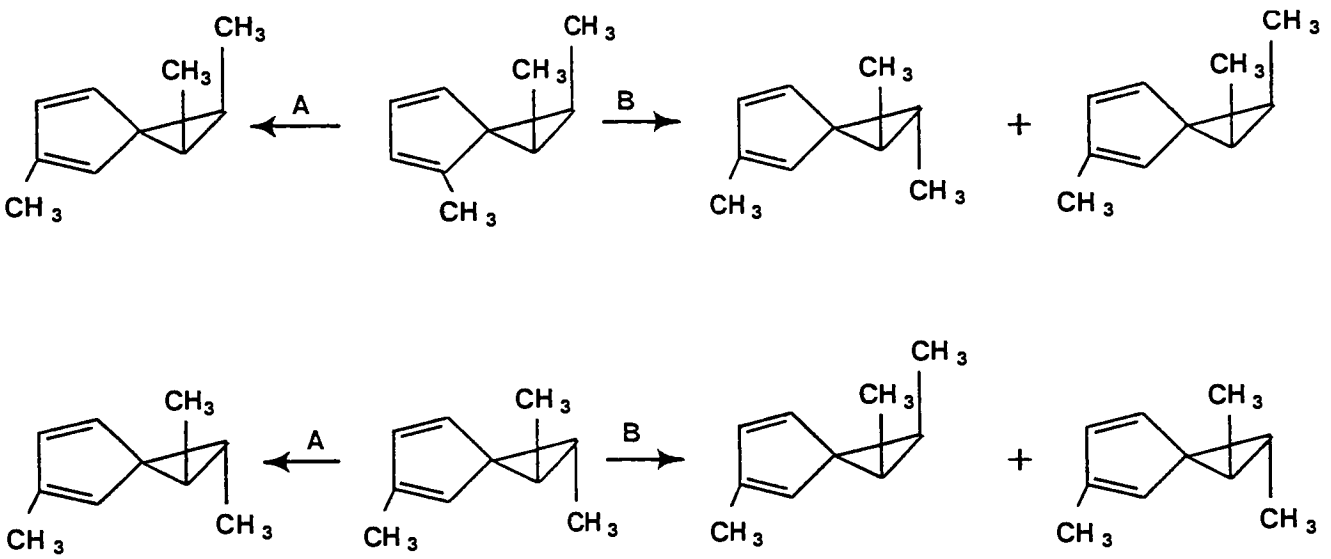
No volatile products other than 36 or 37 were detected in the static gas phase pyrolysates, with greater than 90% of the starting material recovered as the isomeric spirodienes 36 and 37. Kinetic determinations yielded an activation energy for the first order disappearance of 36 or 37 of 44 kcal/mole and an activation entropy of +2 ±1.5 e.u. over a temperature range of 513°-543°K. The slightly positive activation entropy was suggested to agree more with the diradical mechanism as postulated by Kloosterziel[15,16] (activation entropy, pathway B, diradical = +3 e.u.), although somewhat lower than values previously reported for geometric isomerisations of cyclopropanes (*cis*-1,2-dideuteriocyclopropane, +13 e.u.[26] and 1-methyl-*cis*-2,3-dideuteriocyclopropane, +10 e.u.[26]). It is interesting to note that this cyclopropane migration almost certainly involves the intermediate bicyclo[3.2.0]heptadiene 10 at some stage in the rearrangement, although this intermediate was previously suggested to arise only in the concerted process[15,16].

The kinetic studies of the thermal interconversion of 4- and 5- methylspirodiene (36) and (37) are not conclusive in delineating the nature of the transition state(s) for these thermal rearrangements. The slightly positive entropy of activation energy can be disputed as evidence for the diradical intermediacy by comparison to activation entropy values for other known diradical processes in similar systems (see above). The possible competitive operation of the diradical and concerted [1,5] sigmatropic methylene migration mechanisms

can be invoked on the basis of the observed activation entropy being an overall average of that for two processes.

The precise mechanism(s) of the thermal rearrangements of spirodienes **9**, **36**, and **37** could be further elucidated through structural labeling as in the 4- and 5-methylspirodienes (**36**) and (**37**) and stereochemical labeling as in a *cis*-(or *trans*-)-2,3-dimethyl spiroheptadiene (Scheme 12).

Scheme 12



Pathway A, demonstrating retention of configuration by the migrating substituent in the structurally rearranged spirodiene, would be strongly indicative of the operation of a concerted [1,5] sigmatropic carbon shift, followed by a similar hydrogen shift. The loss of stereochemical integrity of the structurally rearranged spirodiene of Pathway B would strongly indicate diradical intermediacy. The purpose of the present research is to obtain an appropriately labeled spiro[2.4]hepta-4,6-diene and to compare the relative rates of structural and geometric reorganization.

II. EXPERIMENTAL

Infrared (ir) spectra were recorded on a Perkin Elmer Model 257 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Hitachi Perkin Elmer model R-20 spectrometer equipped with a variable temperature probe and R201SD spin decoupler. Samples for nmr analysis were approximately 10% (v/v) in deuteriochloroform or hexadeuteriobenzene, with approximately one per cent tetramethylsilane (tms) as internal standard. All chemical shifts are reported as parts per million (ppm = δ) downfield from tms. Multiplicity designations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Gas liquid chromatography (glc) analyses were performed on Varian 1520B instruments equipped with matrix or linear temperature programmers and thermal conductivity detectors. Commercial columns were obtained from Varian Associates. Columns were also prepared in this laboratory according to the procedure given by Dal Nogare and Juvet[27]. All columns used are listed in Table 3; all glc conditions are presented in Table 4. Retention times (t_r) are measured from injection unless otherwise specified. Quantitative analyses of all spirodiene mixtures were accomplished with a Leeds and Northrup model Speedomax G, 0 1 millivolt recorder equipped with a Disc chart integrator. Equivalent detector response factors for all compounds were assumed. Baseline drift was compensated for during integration.

Table 3. GLC Columns used for Preparative and Analytical Scale Analyses

Column Number	Stationary Phase (% by weight)	Support	Column Dimensions	Tube Composition
1	Carbowax 20M (15%)	30/60 Chromosorb W	10' x 3/8"	Aluminum
2.	DC - 710 (15%)	30/60 Chromosorb W	10' x 3/8"	Aluminum
3.	Carbowax 20M (20%)	60/80 Chromosorb W	15' x 1/4"	Copper
4.	SE-30 (20%)	60/80 Chromosorb W HMDS	20' x 1/4"	Copper
5.	Carbowax 20 M (20%)	70/80 Celite 545AB[a]	50' x 1/4"	Copper
6.	SE - 30 (20%)[b] Carbowax 20M (20%)[c]	60/60 Chrom W[b] HMDS 70/80 Celite[a,c] 545AB	6' x 1/4"	Copper

a. Anachrom Laboratories. b. First four feet of column. c. Final two feet of column.

Table 4. Conditions for Analytical and Preparative Scale GLC.

Conditions	Column	Column Temperature °C	Injector Temperature °C	Detector Temperature °C	Detector Current ma	Attenuation	Helium Flowrate ml/min
A	1	150	190	250	150	512	60
B	3	100[a]	220	205	150	128	54
C	5	175	225	190	146	64	67
D	5	180	225	190	170	32	67
E	5	185	260	220	175	2	65
F	5	185	250	200	200	8	67
G	5	30	200	200	150	1	30
H	1,2	168	200	190	150	Variable	60
I	2	150[b]	240	200	125	512	60

a. Matrix temperature programmed: 100°C for 2 min 8°/min for 2 min.; 4°/min. to 160° and hold.
b. Matrix temperature programmed: 150° for 2 min; 15°/min. to 210° and hold.

Pyrolysis tubes of the Carius type were manufactured by Blaessig Glass, Inc., 200mm x 4mm I.D., 2mm wall, Pyrex. Temperature control of the pyrolyses carried out in the chromatograph column oven was ± 0.5°C (Varian 1520B; linear programmer) operated in the isothermal mode.

Tetrahydrofuran, sodium azide, sodium amide and pentane were reagent grade as supplied by Fisher Scientific Co. and were used with no further purification. The 1,3,4-dibromobutane and p-toluenesulfonyl chloride were used as obtained from Eastman Organic Chemicals. The *cis*-2-Butene (CP, 95%) was obtained from Rochester Welding Co.; glc (column 5, conditions G) showed only one peak, t_r = 18.1 minutes from air. Cyclopentadiene and methylcyclopentadiene dimers were used as obtained from Aldrich Chemical Company.

Spiro[4.4]nona-1,3-diene[28] (40). Dry tetrahydrofuran, 250ml, was added to a 500ml three neck round bottom flask fitted with nitrogen inlet, pressure equalizing addition funnel, reflux condenser and magnetic stirrer. Sodium amide, 20g (0.5mole), was added with stirring. Cyclopentadiene, 17g (0.25mole). prepared by destructive distillation of the dimer[29] (fraction boiling at 38°-40°C collected), was added dropwise over 15 min. A solution of

45.5g (0.25mole) 1.4-dibromobutane in tetrahydrofuran, 1:1(v/v) , was added dropwise over 15 min. and was accompanied by heat evolution. The mixture was stirred and allowed to cool overnight. The organic layer was decanted, insoluble salts dissolved in a minimum quantity of water and extracted with three 75ml portions of 20-40° petroleum ether. The extracts were combined with the organic layer and washed successively with 50ml portions of water, 10% HCl and water. After drying over anhydrous magnesium sulfate and filtering, excess pentane solvent was removed from the filtrate by fractional distillation, discarding the fraction boiling at 35-61°C, retaining approximately 150ml of undistilled material. Distillation of the concentrate yielded three fractions: fractions 1 and 2 were discarded as containing mostly tetrahydrofuran (nmr superimposible with that of an original sample); fraction 3, 10ml, 30-100°C, 2mm, pale yellow oil. Analysis of the oil by glc (column 1, conditions H) showed six major components. The liquid spirodiene 40 was first isolated from glc preparations using the above conditions (t_r = 5.5 min from air). Spiro[4.4]nona-1,3-diene (40), 3.6g (14%); nmr($CDCl_3$), δ1.40-2.30(m,8H), δ6.10-6.50(m,4H); ir,40, (NaCl):3110, 3085, 3070, 3050, 2960, 2875, 1830, 1640, 1515, 1450, 1375. 1320, 1305, 1090, 1065, 1008, 975, 940, 915, 845, 800, 735cm^{-1}).

p-Toluenesulfonyl Azide, Sodium azide, 14.0g (0.22mole) dissolved in 40ml water was added to 34.0g (0.18mole) of p-toluenesulfonyl chloride partially dissolved in 40ml of 95% ethanol and was stirred for one hour. The oily p-toluenesulfonyl azide layer was separated from the aqueous phase, washed three times with 20ml portions of water and dried over anhydrous magnesium sulfate. Filtration yielded 28.6g (81%) of the azide.

Diazomethylcyclopentadiene, (41). Methylcyclopentadiene was prepared by destructive distillation of the dimer[29] at a temperature of 185°C, collecting the fraction boiling at 76-79°C. A mixture containing 0.1 mole each of methylcyclopentadiene (8.0g) p-toluenesulfonyl azide (19.7g) and diethylamine (7.3g) was prepared. The mixture darkened almost immediately to a deep red-brown color and eventually black-brown after three days at 10°C.

The mixture was poured into 70ml water, causing formation of large amounts of a flocculent brown precipitate. After removal of the precipitate by filtration, the organic layer was separated and retained. The solid was washed with 50ml of pentane which was combined with the filtrate. The aqueous fraction was extracted with three 25ml portions of pentane. The pentane extracts were combined with the previously separated organic layer. The organic fraction was washed with seven or eight 100ml portions of water until the final wash was neutral to litmus. After drying with anhydrous magnesium sulfate, and filtration, the organic fraction was concentrated at aspirator vacuum and room temperature to a total volume of approximately 25ml. Further purification of the diazo compound **41** was not attempted due to the explosive characteristics of the similar compound, diazocyclopentadiene[30,31,32].

Reaction of Diazomethylcyclopentadiene (41) with cis-2-Butene.

Procedure A. A variable amount of the diazomethylcyclopentadiene 41 - pentane mixture was added to the Hanovia reaction vessel equipped with jacketed quartz insert, magnetic stirrer and two cold finger condensers. The dry ice-cooled apparatus was charged with approximately 250ml of *cis*-2-butene. The cold finger condensers were filled with dry ice and cooling water at maximum pressure was directed through the cooling jacket of the quartz insert. To lower the temperature of the inlet cooling water, thirty feet of the water inlet tubing was immersed in a methanol-ice cooling bath. Photolysis time was five hours: the light source was an high-pressure Hanovia mercury arc lamp (type 679A-36), 450 watts, 7.5 inch arc. The lamp was placed in an open tube Pyrex filter. optical cutoff at 280-300nm. in the lamp well of the quartz insert.

Procedure B. The Hanovia apparatus was charged with *cis*-2-butene and reactants and equipped exactly as in Procedure A (see above), except that the lamp well in the quartz insert was filled with an alcohol-ice mixture at -10°C and the cooling jacket was filled with technical grade chloroform. The apparatus was placed in the Rayonet photochemical minireactor for external irradiation of the reaction mixture through the Pyrex exterior wall of the Hanovia apparatus. The Rayonet was equipped with either 3500Å or 2537Å lamps and photolysis time was varied from 8 to 17 hours (Table 5).

For Procedures ***A*** and ***B*** dry ice was added to the cold finger condensers at thirty-minute intervals. Magnetic stirring at a moderate rate was essential to prevent "bumping out" of *cis*-2-butene. The alcohol-ice mixture in Procedure B was replenished by aspirating out all liquid, filling the well with ice and adding pre-cooled alcohol.

After photolysis was terminated, the *cis*-2-butene was allowed to evaporate by removing the cold finger condensers and fitting the Hanovia apparatus with two gas outlets. The gas was condensed into a pre-cooled (dry ice), disassembled lecture bottle (approximately 400ml capacity). The reclaimed *cis*-2-butene was suitable for subsequent reactions.

Pentane and any residual *cis*-2-butene was removed by transferring the reaction mixture into a 500ml round bottom flask and the solvents distilled from the mixture at a pot temperature of 50°C and aspirator vacuum on the Rinco rotary evaporator apparatus.

Table 5. Photolysis Reaction Parameters for Reaction of Diazo Compound **41** with *cis*-2-Butene.

Reaction	Irradiation Time[a-c] (hours)	Diazo Compound **41** g/ml (pentane[d,c])
I	5[a]	5.6/25[d]
II	8[b]	10.9/25[d]
III	12[b]	21./25[d]
IV	12[b]	10./25[d]
V	18[c]	6./50[e]
VI	11[c]	3./50[e]
VII	12[c]	3./50[e]

a. Hanovia high pressure 450 watt mercury arc lamp (7 1/2").
b. Rayonet photochemical minireactor. 3500Å bulbs.
c. Rayonet photochemical minireactor. 2537Å bulbs.
d. Products purified by vacuum distillation prior to preparative scale glc analysis.
e. Products purified by alumina filtration (1" x 1" I.D. column 100ml pentane elution volume.) prior to preparative scale glc analysis.

Purification of 42,43,44,45, and 46. Conditions such as the amount of diazo compound **41**, its purity and concentration in pentane, radiation intensity, wavelength and duration of irradiation were varied extensively. Table 5 summarizes these variations. Concentrated oils resulting from reactions II through IV were further purified by vacuum distillation (100°C, 0.25 torr). The distillate from reaction II provided enough trimethyl spirodienes (**41-46**) for tentative identification (see below). Reactions III and IV failed to yield any trimethyl spirodienes (**42-46**) after vacuum distillation, although glc peaks corresponding to the trimethylspirodienes **42-46** were present in the crude oil prior to vacuum distillation. During these distillations of the products of Reactions III and IV, formation of a brilliant yellow solid in the dry ice trap was observed. The melt of this solid was a red oil (m.p. less than 0°C) and ir analysis of the oil showed a strong absorption band at 2070cm^{-1}. These are all characteristics of the similar compound, diazocyclopentadiene[33]. Concentrated oils resulting from reactions V through VII were purified by alumina filtration (column one inch I.D. by one inch length; total elution volume, 100ml pentane). The resultant red solutions were concentrated at aspirator vacuum to a total volume of approximately 10ml or less, and kept under nitrogen at -10°C before and during preparative scale glc. Successive glc

preparations and analyses are summarized under the respective reactions (see below).

Reaction 1. Crude preparative glc to isolate trimethylspirodienes **42-46** from lower and higher molecular weight substances (column 1, conditions A) yielded 0.94g of a yellow oil. The oil was subsequently repurified by preparative scale glc to isolate each separable component (column 3, conditions B). The *trans* 1,2,5-trimethylspiro[2.4]hepta-4,6-diene. **46**: nmr ($CDCl_3$), δ 1.28 (d,6H, J = 8Hz), δ 1.55 - 1.89 (m,2H), δ 6.12 - δ 6.42 (m,2H): ir (NaCl). 3050, 3000, 2955, 2930. 2870, 1595. 1515, 1495, 1450. 1380, 1265, 1175, 1095, 1080. 1040, 999cm^{-1}. Spectra were superimposible with those obtained by D. S. Youngs[34] for independently prepared *trans*-5-spirodiene **46**. Other glc peaks collected from this preparation of Reaction I were of insufficient quantity for analysis.

Reaction II. Vacuum distillation yielded 3.1g of a pale yellow oil. Preparative scale glc (column 5. conditions C) showed 8 peaks:

The *trans*-2,3,5-trimethylspiro[2.4]hepta-4,6-diene **46**, or ("trans-5-spirodiene isomer" hereafter), t_r = 46.4 min.;

The *cis*-2,3,5-trimethylspiro[2.4]hepta-4,6-diene **43 or 44**, or ("earlier *cis*-5 isomer" hereafter), t_r = 49.5min.;

The *trans*-2,3,5-trimethylspiro[2.4]hepta-4,6-diene **45** ("*trans*-**4**-spirodiene isomer" hereafter), t_r = 52.5 min.;

The *cis*-2,3,4-trimethylspiro[2.4]hepta-4,6-diene **42** or ("*cis*-**4**-spirodiene isomer" hereafter), t_r = 59 min.;

And the other *cis*-2,3,5-trimethylspiro[2.4]hepta-4,6-diene, **43** or **44** ("later *cis*-5-spirodiene isomer" hereafter), t_r = 68min., from injection.

The overall yield of trimethylspirodienes was estimated to be 21% of theory; for *cis*-trimethylspirodienes, it was estimated to be 16% of theory. Earlier *cis*-5-spirodiene, **43** or **44**; nmr ($CDCl_3$), δ 1.15 -1.50(m, 6H), δ 1.50 -2.20(m, 5H), δ 2.03(d,3H), δ 5.85 6.10(m,2H), δ 6.15 - 6.35(m, 1H); ir(NaCl): 3060, 3020, 2970, 2930, 2880, 2740, 2760, 1710. 1600, 1515, 1455, 1410, 1390, 1345, 1265. 1190, 1095, 1060, 1020, 1000, 890, 810, 790, 700, 655cm^{-1}. The *cis*-4-spirodiene, **42**; nmr($CDCl_3$), δ 1.15 -1.45(m, 6H), δ 1.55 - 2.10(m, 5H), δ 1.64(d,3H), δ 6.00 -6.30(m, 2H), δ 6.48 6.67(m, 1H); ir(NaCl); 3115, 3080, 3020, 2970, 2940, 2890, 2740, 2760, 1805, 1615, 1595. 1515, 1505, 1470, 1450, 1410, 1390, 1345, 1330, 1265, 1235, 1170, 1135, 1085, 1030, 1020, 1005, 970, 915, 830, 795, 775, 715cm^{-1}. later *cis*-5-spirodiene, **44** or **43**; nmr($CDCl_3$), δ 1.27 - 1.45 (m, 6H), δ 2.02 - 2.40(m, 5H), δ 2.06(d. 3H), δ 5.73 - 5.90 (m, 1H), δ 6.20 - 6.45(m, 2H). (ir not obtained.)

Reactions III and IV. Analytical glc (column 5, conditions E) showed that the crude concentrated oil before vacuum distillation contained compounds of retention times (t_r) corresponding to trimethylspirodienes **42** **46**. The vacuum distillate contained no volatile

components to glc. One plausible explanation for this occurance is that excess diazo compound **41** caused decomposition and/or polymerization of the products when the diazo containing mixture was subjected to elevated temperatures (above 100°C) and reduced pressures of 0.25 - 0.1 torr.

Reactions V-VII. The concentrated oils from the reactions were purified by alumina filtration (see above), pooled and concentrated to a total volume of approximately 10ml. The total yield of *cis*-4-spirodiene **42** from preparative scale glc (column 5, conditions C) of this oil was approximately 0.150ml. The concentration of diazo compound **41** in the oil was estimated to be 15% by analytical scale glc (column 5, conditions D). Tarry deposits in the injection port area of the gas chromatograph apparently resulted from repetitive injections of this mixture and strongly indicated thermally induced decomposition of diazo compound **41**. *in situ*. The analytical scale glc yielded an estimate of 25% for cis-4-spirodiene **42**.

Thermal rearrangement of *cis*-4-spirodiene *42*. A standard mixture was prepared for all pyrolyses containing 150μl **42** and 40μl n-butylbenzene as internal standard. To each of seven Carius tubes was added 6μl of the standard mixture and to each of two Carius tubes 14μl was added for extended pyrolyses. Each tube was evacuated to 0.25 torr while at liquid nitrogen temperature and flame sealed within two minutes after evacuation. The gas phase pyrolyses were accomplished by placing the tubes in the Varian 1520B gas chromatograph column oven, heated isothermally at 225°C (498°K). A time period of from five to ten minutes is assumed to be necessary for the tube and contents to reach temperature equilibrium. The composition of each mixture was determined by analytical glc analysis (column 5, conditions F) of the pyrolysate diluted in 60μl pentane. Dilution of the pyrolysate facilitated reproducibility of repetitive injections at the highly sensitive conditions used for analysis. The data for these determinations are presented in Table 6 along with calculated first order rate constants based on the disappearance of *cis*-4-spirodiene **42**.

Table 6. Thermal Rearrangement Experimental and Kinetic Results

Time (hours)	%42	%46	%45	%43 + 44	% Decomposition	k x 10^5 sec^{-1}	$t_{1/2}$
0	93.3	0	8.7	<0.1	0	-	
1.5	79.5	2.7	17.9	<0.1	3.0	3.50	5.4
2.17	78.5	3.0	18.5	<0.1	0	2.00	10.0
3.0	75.7	4.6	19.7	<0.1	0	1.49	12.6
4.5	68.0	5.5	26.5	<0.1	0.8	2.02	9.3
5.5	61.1	8.5	30.4	<0.1	0	2.03	9.5
6.5	58.2	9.5	32.3	<0.1	0	2.03	9.5
20.0	45.3	19.3	35.4	<0.1	4.9	1.08	17.9
22.0	44.6	19.7	35.6	<0.1	8.0	1.04	18.5
50.2	29.8	39.8	30.4	<0.1	81.0[a]	1.55	12.4
70.3	31.1	36.8	32.3	<0.1	69.5	0.905	21.0

a. Foreign matter from vacuum tubing accidentally introduced into sample during sealing of vial is probable cause of high decomposition rate.

RESULTS AND DISCUSSION

I. Introduction

The purpose of this research was to synthesize an appropriately substituted spiro[2.4]hepta-4,6-diene. structurally labeled on the five-membered ring and stereochemically labeled on the three-membered ring. The thermal rearrangement mechanism would hopefully be determined by measurement of the relative rates of stereochemical isomerization in the cyclopropane ring and structural reorganization in the cyclopentadiene ring. The results of this study should aid materially in the elucidation of the mechanism of the 1,5-alkyl migration proposed as the rate determining step in the thermal equilibration of the 4- and 5-methylspiro[2.4]hepta-4,6-diene.[25] As reported earlier, the mechanism of the thermally promoted 1.5- migration of alkyl groups in cyclopentadienes is sensitive to the precise pattern of substitution in the cyclopentadiene: the concerted, biradical or sometimes both mechanisms apparently being operative.

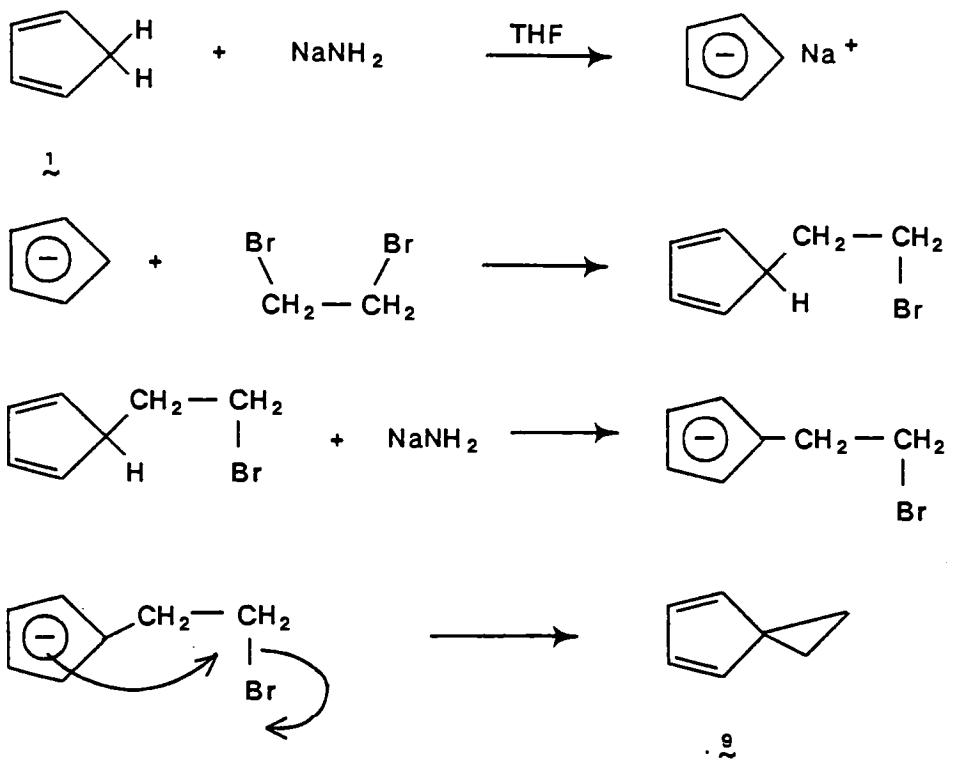
In order to permit the most direct comparison of the mechanistic results obtained in the present study to those reported[25]. it was desired to design a spirodiene system with minimal structural perturbation as compared to the 4- and 5-methylspiro[2.4]hepta-4,6-dienes. The ideal stereochemical label for the cyclopropane ring would then be deuterium; however, the synthetic difficulties dictated rather strongly against this approach. The use of methyl labels appeared to be synthetically feasible and to provide a relatively small energetic and mechanistic perturbation. Furthermore. it appeared that isomer separation and characterization in the 2,3,4- and 2,3,5-trimethylspiro[2.5]hepta-4,6-dienes would be simpler than in the correspondingly deuterated analogs.

As a general rule, the *cis*- configuration of the methyl groups in simple cyclopropanes[26,27] is thermodynamically less stable. The cyclopropane moiety of the spirodiene system is expected to, at least a small extent, be consistent with the above observation. For that reason, *cis*-methyl geometry of the cyclopropane ring is considered an appropriate label in order to distinguish between kinetic and thermodynamic control of the product stereochemistry.

II. Synthesis of 2,3,4- and 2,3,5- trimethylspiro[2.4]hepta-4,6-dienes.

The synthetic used route will be treated first, followed by discussions of characterization of the products 42-46, and finally, the thermal rearrangement. Two synthetic routes have been used for the synthesis of the spirodiene 9 ring structure. The first route in this research (Scheme 13) is referred to as the "dibromide route".[28]

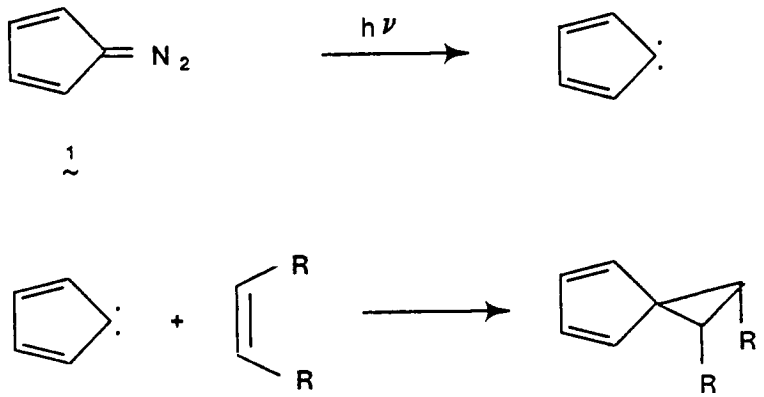
Scheme 13.



The success of this route relies on the comparative ease of cyclopentadienide formation and its nucleophilic character towards the 1,2-dibromoethane, involving intra-molecular displacement of bromide to yield the cyclopropane moiety. Complications of this route, however, when applied to the desired methyl labeled cyclopropanes are several. The overall yield of the 1,2-dibromoethane synthesis[34] was 65%. The same synthesis, except using methylcyclopentadienes (2a-2c) resulted in a 35% overall yield. The synthesis of the 2,3-dimethylspirodienes 38 and 39, *cis*- and *trans*- respectively, requires the use of the secondary dibromide, 2,3-dibromobutane, resulting in an overall 9% yield. The trimethyl spirodienes 45 and 46 (*trans*-4 and *trans*-5) synthesized from methylcyclopentadienes (2a-2c) and 2,3-dibromobutane were recovered in a maximum yield of only 4%. The more favorable base promoted bimolecular elimination of the secondary dibromide is presumably largely responsible for the significant lowering of yields in the synthesis.

The alternate route, initially reported by Moss and Pryzbyla[36], is the cycloaddition of cyclopentadienylidene to the appropriate olefin (Scheme 14).

Scheme 14.

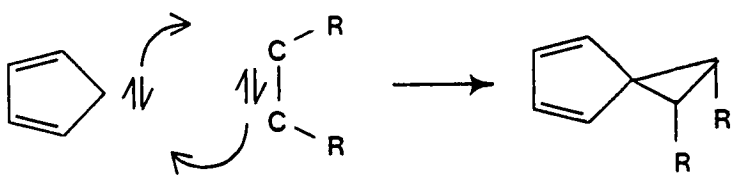


The researchers found this reaction to be largely stereospecific with the geometry of the olefin reflected by the geometry of the product spirodiene. A *cis*-labeled olefin yielded a three membered ring in the product spirodiene with predominantly the *cis*-configuration. Small amounts of *trans*-spirodienes were observed in their syntheses (1-8%). The non-stereospecific component of the reaction was extensively investigated. The two likely sources of *trans* product from a *cis* olefin were thought to be either a substantial triplet carbene population or a secondary photoisomerization of the product. Singlet carbene, where the lone pair of electrons are spin paired, is well known to add stereospecifically to an olefin[36,37]. When the non-stereospecific component becomes significant, a number of factors must be considered. The secondary photoisomerization of the product is considered first, followed by loss of stereochemistry during the cycloaddition reaction.

It is our observation that the non-stereospecific component of the reaction in this research did not vary with the wavelength, intensity or duration of light used in the photolysis reaction (Table 5, above). The overall *cis* to *trans* ratio of 4:1 did not vary when a high pressure mercury arc lamp, 2537A low pressure lamp or 3500A lamps were used. The photolysis time was varied from 5 to 18 hours. The concentration of diazomethylcyclopentadiene (41) was also varied. The data indicate that secondary photoisomerization is not a significant process.

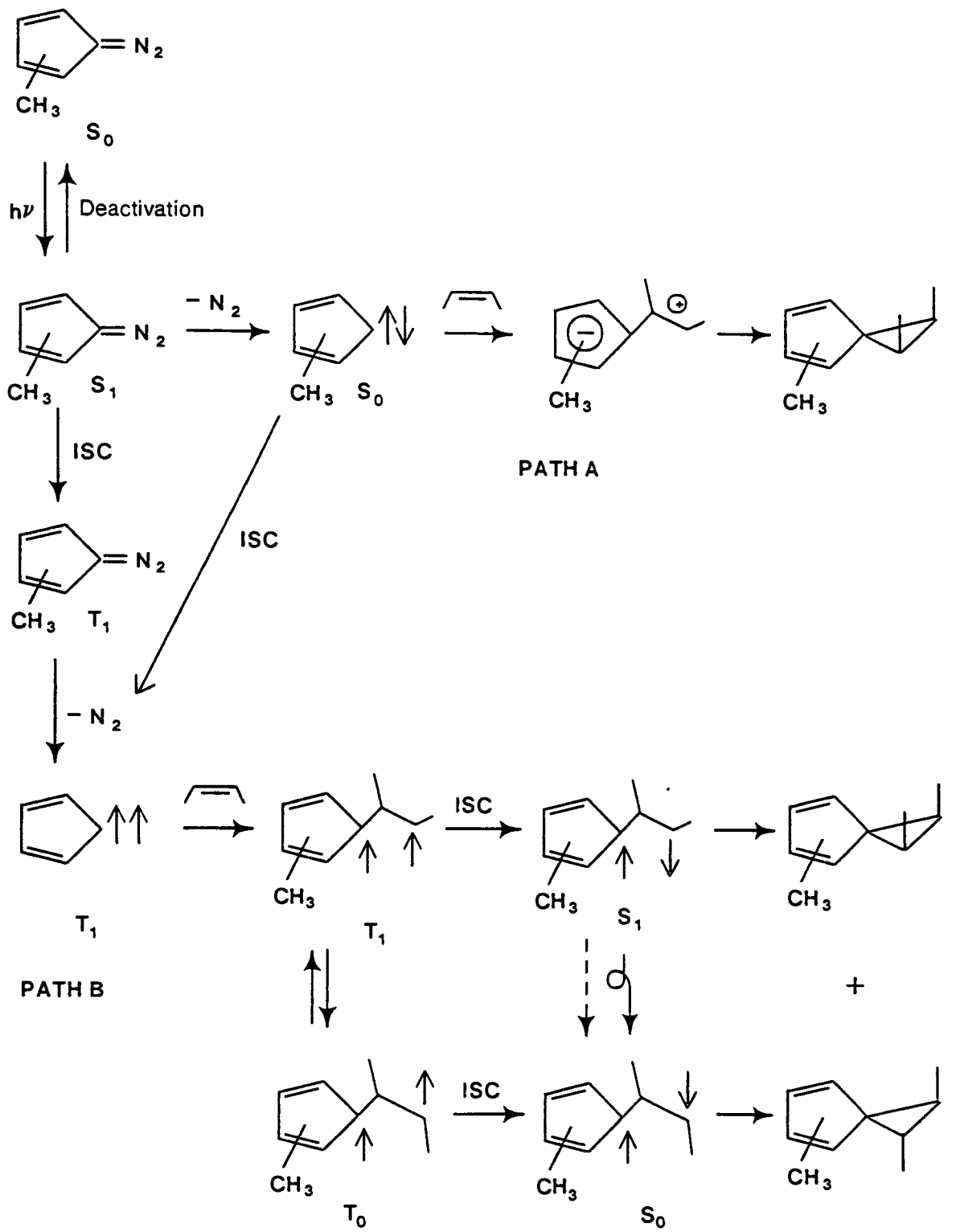
The cycloaddition reaction involving intermediate carbenes is complicated by the possible spin states of the intermediate. The singlet carbene, once formed, can react immediately with olefin reagent, presumably in a concerted fashion (Scheme 15) to yield total retention

Scheme 15



of stereochemistry. However, the singlet carbene may also react in a stepwise, as opposed to a concerted manner, to give the same effect. (Scheme 16).

Scheme 16



The stepwise mechanism that yields retention of stereochemistry assumes that the rate of ring closure (final step) is much faster than the rate of C-C bond rotation, since the soon-to-be-bound electrons are already spin paired. The analogous reaction using diazomethane is known to be entirely stereospecific.[36,37] Skell's hypothesis predicts that a singlet carbene will add in a concerted fashion with both of the three ring bonds forming simultaneously, disallowing any changes in the stereochemistry of the olefin. The present research involves an intermediate carbene that can be stabilized by an adjacent conjugated *pi* system resulting in the Huckel number of *pi* electrons necessary for aromaticity with the carbene electrons. Based on this observation, it is proposed that the lifetime of the carbene intermediate may be significantly longer than in the case of methylene. If a stepwise cycloaddition reaction is operative with the singlet state of the carbene, it is possible that the somewhat slow C-C bond rotation may be more competitive with the final ring closing step. Other possibilities for stereochemical scrambling remain.

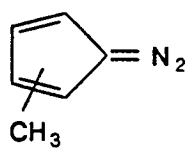
Another process that a singlet carbene can undergo is intersystem crossover to the T_1 triplet state assuming that the lifetime of the singlet carbene is long enough to permit this comparatively slow process to occur. Again, electron delocalization of the carbene through the conjugated *pi* system of the five ring is invoked to rationalize this assumption. The triplet state is known to result in loss of stereochemistry since, once the initial bond between the carbene and the olefin is formed, one electron must undergo spin inversion for the subsequent ring closure bond to form. The rate of electron spin inversion is considered to be slow and competitive with the C-C bond rotation step that attends stereochemical scrambling of the products. The overall reaction rate of triplet carbene with olefin should be slower than the same reaction with singlet carbene since triplet is at a lower energy. Further, intersystem crossover is a process that may occur at any point in the cycloaddition reaction. The slower the reaction, the more opportunity there is for intersystem crossover to occur and the subsequent loss of stereochemistry becomes more dominant. Factors that stabilize an intermediate also act to reduce the rate of reaction involving the intermediate. The cyclopentadienylidene intermediate is certainly stabilized and it is expected that the cycloaddition reaction of this intermediate relative to methylene is slower. The data acquired in this research indicate strongly that the nonstereospecific component of the reaction is due to intersystem crossover and not secondary photoisomerization.

The ground state of cyclopentadienylidene is known to be triplet[39]. The researchers Moss and Pryzbyla[36] have suggested a reacting singlet electronic configuration in the reaction between cyclopentadienylidene and reagent olefin to form the spirodiene system. Dilution studies to enhance the rate of intersystem crossover relative to cycloaddition between singlet and triplet carbene **47**, carried out in inert matrices of hexafluorobenzene and octafluorocyclobutane, were inconclusive in that there was no enhancement of the *trans*-product yields observed. The authors seem to favor the postulate that the *trans*- product from the photolysis reaction of the diazocyclopentadiene in *cis*-2-butene arises principally

from secondary photoisomerization. The rates of cycloaddition to styrene and 1-hexene are identical which caused the researchers to conclude that the cyclopentadienylidene **47** arising from the photolysis of diazocyclopentadiene is a singlet. This is reasonable when one considers that the styrene system is stabilized by the aromatic *pi* system. whereas the 1-hexene, a terminal olefin, has no such stabilization.

The styrene reaction would be expected to proceed faster if the stability of the olefin were a significant factor. The triplet state of the cyclopentadienylidene intermediate is at a lower energy than the singlet. If the energy of the triplet is at a low enough level relative to the olefin. the cycloaddition reaction rate difference between styrene and 1-hexene would be observed. If, however, the singlet and triplet states are both at much higher energies relative to the olefin, the rates of the cycloaddition reaction rates would not differ significantly. Conversely, if both the singlet and triplet states are relatively low compared to the olefin. again the cycloaddition reaction rates would be similar. Since secondary photoisomerization does not seem to be responsible for stereochemical scrambling in this research. it is presumed that the lifetime of the cyclopentadienylidene intermediate is sufficiently long to permit intersystem crossover to the triplet state and to allow competition between ring closure and C-C bond rotation which allows1 stereochemical scrambling of the final product spirodienes.

The photolysis of diazomethylcyclopentadiene (**41**) had previously been unreported. It is

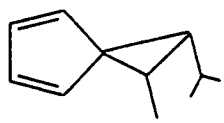


41

reasonable to expect that the methyl group on the cyclopentadiene ring would enhance the diradical character of the intermediate. This would contribute to an expected decrease in the stereoselectivity of the cycloaddition reaction, since the additional stability of the carbene intermediate would contribute again to a longer lifetime and hence the processes that attend stereochemical scrambling (see above).

The results of the photolysis reactions of diazo compound **41** in *cis*-2-butene tend to bear this out. In all cases, regardless of variations of diazo compound **41** concentration or its purity in pentane solution, wavelength and intensity of incident radiation or duration of irradiation. the *cis*- to *trans*- ratio of trimethylspirodiene products **42-46** remained essentially invariant (see above). This ratio was approximately 4:1 (*cis* : *trans*) overall. Total product yield was a maximum of 21%, and was not reproducible. Numerous difficulties were

encountered in the work up of crude products **42** - **46**. These difficulties are attributed to unreacted diazo compound **41** in the product mixture. Moss and Pryzbyla demonstrated that diazocyclopentadiene will thermally decompose in the injection port of a gas chromatograph at a temperature of 192°C in the presence of an appropriate olefin to yield spirodiene products[36]. It is noteworthy that this reaction with 4-methyl-*cis*-2-pentene was far less stereospecific (3:1, *cis* : *trans*) which was attributed to a thermally excited spirodiene **48** which could subsequently rearrange to the *trans* analog. In this research, product mixtures purified by alumina filtration and concentrated at aspirator vacuum, were virtually



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free of all but traces of reagent olefin. It is logical, therefore, to conclude that any diazo compound **41** that should decompose in the gas chromatograph during glc preparation could react with spirodiene products **42** - **46** either *via* a cycloaddition to the conjugated diene system or a carbon hydrogen bond insertion reaction, ultimately resulting in polymerization of the desired products. Black, tarry residues were observed in the injection ports of the gas chromatographs following all glc preparations. Efforts to separate diazo compound **41** from the crude reaction product via column chromatography (alumina) and pentane elution were fruitless. Extended photolysis times and reduction of initial diazo compound **41** concentration were of no help either. Nevertheless, a small amount of spirodienes **42** **46** was obtained for spectral characterization and thermal rearrangement studies.

III. Characterization of the trimethylspirodienes: ***cis***-2,3,4-trimethylspiro[2.4]-hepta-4,6-diene; (42); ***cis***-2,3,5-trimethylspiro[2.4]hepta-4,6-diene (43 or 44); ***cis***-2,3,6-trimethylspiro[2.4]hepta-4,6-diene (44 or 43); ***trans***-2,3,4-trimethyl-spiro[2.4]hepta-4,6-diene (45); and ***trans***-2,3,5-trimethylspiro[2.4]hepta-4,6-diene (46).

The characterization of the trimethylspirodienes synthesized during this research is based upon experimental evidence including, but not limited to, spectrometric measurements. The synthetic pathway from diazomethylcyclopentadiene (41) and *cis*-2-butene leads to spirodiene products containing a single methyl group on the five membered ring and two methyl groups on the three membered ring in the 2,3 positions (42→46). Single methyl substitution of the five ring is best characterized by observing spectrometric perturbations resulting from monomethyl substitution in 4-methylspiro[2.4]hepta-4,6-diene (36) and 5-methylspiro[2.4]hepta-4,6-diene (37). Similarly, *cis* and *trans* substitution of the adjacent 2.3 carbons of the cyclopropane ring are best characterized by observing the spectral characteristics of *cis*- and *trans*-2,3-dimethylspiro[2.4]hepta-4,6-dienes (38 and 39). This technique allows independent observation of the spectral effects of such substitutions in the absence of the other. Once such effects have been sufficiently characterized, the more complicated spectral patterns of the trimethylspirodienes may be more readily understood.

The characterization of trimethylspirodienes depends in part upon experimental evidence as well as spectrometric. Such data includes. but is not limited to, gas chromatographic retention time and synthetic route, including starting materials that led to the formation of the compounds under scrutiny. The two *trans* isomers *trans*-2,3,4-trimethylspiro[2.4]hepta-4,6-diene (45) and *trans*-2,3,5-trimethylspiro[2.4]hepta-4,6-diene (46) are in part characterized in this manner.

The entire characterization argument for the three previously unknown trimethylspirodienes, *cis*-(2,3,5)-trimethylspiro[2.4]hepta-4,6-diene (43 or 44), cis-2,3,6-trimethylspiro[2.4]hepta-4,6-diene (44 or 43) and cis-2,3,4-trimethylspiro[2.4]hepta-4,6-diene (42) depends upon previous and current experimental, synthetic, and spectrometric evidence. Even so, despite the great preponderance of such evidence, the absolute identification of the two compounds 43 and 44 remains incomplete and vague. The difficulty arises in determination of the relationship of the five ring methyl group relative to the *cis*-2,3 dimethyl label of the cyclopropane ring.

Monomethyl substitution of the five ring in spiro[2.4]hepta-4,6-dienes is accomplished by the use of methylcyclopentadiene in syntheses of the compounds[ref]. Careful inspection of the molecule shows (in Figure 3) that only two isomers are predicted in such syntheses, since a plane of symmetry exists in the plane of the cyclopentadiene ring. The plane of the

cyclopropane ring, which is perpendicular to the five ring plane, is no longer a plane of symmetry once the five ring is monomethyl substituted.

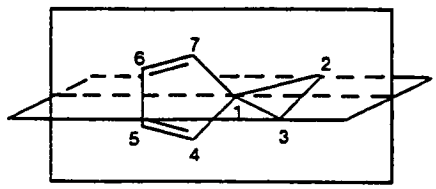


Figure 3. Planes of Symmetry and Numbering System of the Spiro[2.4]hepta-4,6-diene (9) molecule.

As long as the three ring plane is a plane of symmetry, there are no differences between positions 4 and 7 or positions 5 and 6. Therefore, a methyl group on the five ring in the 4 or 7 position is a 4-methyl spirodiene and similarly 5 or 6-position methyl substitution becomes only 5-methylspirodiene.

The synthetic pathway to these compounds are *via* methylcyclopentadiene (2) and 1,2-dibromoethane in what appears to be a two-step biomolecular substitution reaction to yield the spiro[2.4]heptadiene ring system. Methylcyclopentadiene 2 is known to form the anion[3,8,10,11] and to rapidly isomerize under alkaline conditions to a mixture of 1-,2-, and 5-methylcyclopentadiene (2a-c), presumably through the cyclopentadiene anion (Figure 1; see above). The spiro[2.4]hepta-4,6-diene ring system is a 5,5 disubstituted cyclopentadiene. Only two spirodienes are found in the reaction mixture and, based upon spectral evidence, they are identified as 4- and 5-methylspiro[2.4]hepta-4,6-dienes 36 and 37.

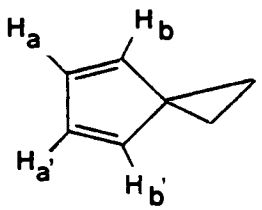
The nmr data (Appendix A) for these compounds, in comparison to the nmr spectrum of the unsubstituted parent spirodiene 9 (Appendix A, Spectrum 1), demonstrate the necessary signals and correct proton integration for the desired compounds (36 and 37). The spectrum assigned to 5-methylspiro[2.4]hepta-4,6-diene (37) (Appendix A, Spectrum 2) has the following elements: singlet at δ1.5 integrating for 4H assigned to cyclopropyl protons; a doublet at δ2.05 integrating for 3H and assigned to the methyl group; multiplets at δ5.7, δ6.05, and δ6.35 integrating for 1H each and assigned to the olefinic hydrogen.

The two furthest downfield multiplets demonstrate mirror symmetry similar in pattern and chemical shift to the unsubstituted spirodiene 9. The assignment of 5-methyl substitution to this spectrum is based upon comparison to the spectrum of the other monomethyl spirodiene from the reaction. which demonstrates a multiplet in the region of δ1.2 to δ1.6 integrating for 4 protons (Appendix A. Spectrum 3). This additional multiplicity is explained by the proximity

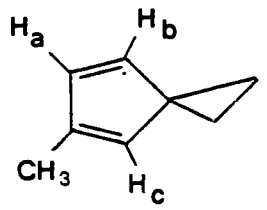
of a 4-methyl group directly adjacent to the three ring and directed at one side of the ring (Figure 3). The proximity of this methyl group to the protons on the three membered ring apparently sufficiently perturbs the magnetic environment of these two protons to make them magnetically non-equivalent to the protons and therefore induces the observed proton-proton coupling.

The methyl group in the 5-methyl spirodiene **37** is directed away from the cyclopropane ring, and no methyl induced cyclopropyl proton non equivalency is expected.

The signal assigned to the methyl group in 4-methylspirodiene **36** is at δ1.7 and is integrated for 3 protons. The olefinic pattern of **36** shows one multiplet integrating for one proton at δ6.45 with the same mirror symmetry in **9** and **37** and multiplets at δ6.0 and δ6.18 showing portions of the remaining mirror symmetry signal (Figure 4).



9



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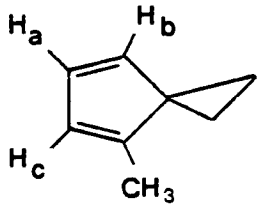

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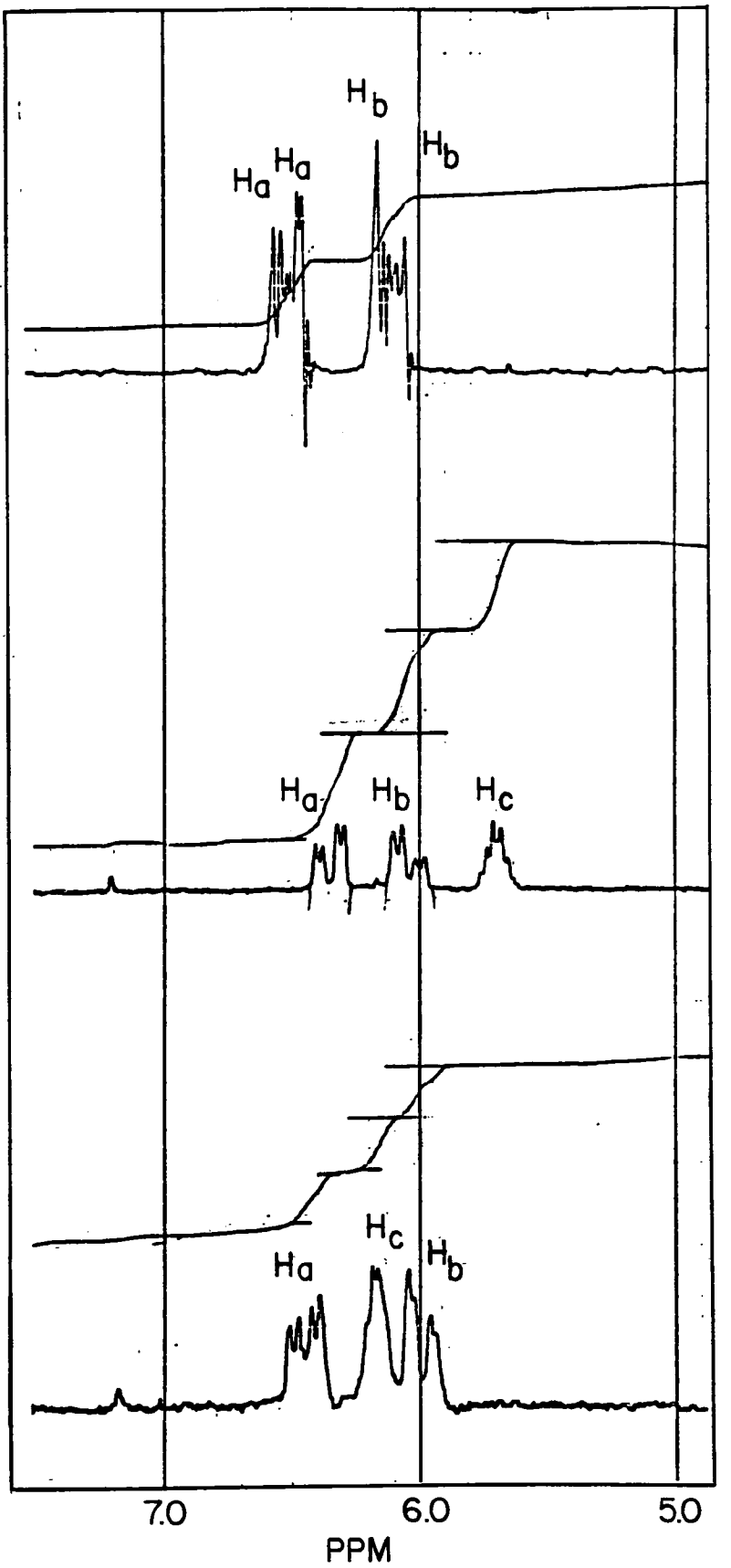


Figure 4. 60 MH_3 NMR Signals of Olefinic Regions of Spiro [2,4] hepta - (4,6) - diene 9 and 4 and 5 - Methyl spiro [2,4] hepta - (4,6) - dienes 36 and 37

On the basis of the forgoing arguments, the assignment of the spectra to the respective compounds **36** and **37** is made. It remains to make any additional assignments of other signals in these spectra and in unsubstituted spirodiene **9**. The signals attributed to the protons at positions 4- and 7- in the spirodiene system **9** may be assigned by contrasting the only two possible assignments. One assignment is reasonable; the other is not.

The olefinic AA'BB' signals in **9** (Figure 4) are reduced to an ABC pattern in the 4- and 5-methyl spirodienes **36** and **37**. The mirror symmetry portion of the ABC pattern in 5-methylspirodiene **37** is comprised of two multiplets, each integrating for one proton. These multiplets are assigned to H_a and H_b on the opposite side of the ring from the methyl substituent. The remaining multiplet at δ5.7 is assigned to H_c.

The olefinic patterns of spirodiene **9** are assigned as follows: The downfield multiplet at δ6.5 (2H) is H_a and $H_{a'}$; the upfield signal at δ6.1 (2H) and H_b and $H_{b'}$. The result of substituting a methyl group for a proton in position 5 (H_b), as in 5-methyl spirodiene **37**, is to cause the adjacent 4 proton in the upfield signal of **9** to be shifted out of that multiplet to δ5.7, a shift of ca. δ0.48. The remaining 4 proton on the opposite side of the ring from the methyl group is presumably minimally perturbed and its signal is observed at δ6.1 (1H). The 5-proton in **37** (H_a) adjacent to the methyl group is also seen to be shifted upfield relative to **9** approximately 0.15δ.

These assignments are applied to spirodiene **36**. A 4 proton is substituted by a methyl substituent. The 5-proton (H_c) adjacent to the methyl is shifted out of the downfield multiplet of **9** at δ6.5 to δ6.2, a shift of approximately 0.3δ.The signal almost overlaps with the signal due to the 4-proton, H_b, on the opposite side of the ring from the methyl group. The proton H_b is minimally perturbed by the methyl group and is observed at δ6.0 (1H), essentially the same as the 4 protons in spirodiene **9**. The 5 proton, H_a, across the ring from the methyl group, is shifted upfield relative to **9** only 0.1δ, again a comparatively small effect.

All shifts attributed to the methyl group as a result of the assignments are in the upfield direction and relatively small in magnitude ranging from almost no perceptible difference to 0.4δ.

The alternate argument is based upon reversal of the assignments in spirodiene **9**. The signals due to the 5- protons, H_a and $H_{a'}$ are attributed to the upfield multiplet at δ6.05; the 4-protons H_b and H_b' are assigned the downfield multiplet. The olefinic signal of 5-methyl spirodiene **37** is assigned similarly as follows: The protons on the opposite side of the ring from the methyl group are assigned to the signals demonstrating mirror symmetry. The remaining 4 proton H_c adjacent to this methyl group is observed at δ5.7, an upfield shift of 0.77δ.

The same reversed assignments are applied to 4-methylspirodiene **36**. The two multiplets demonstrating mirror symmetry are assigned to the protons opposite the methyl group. The remaining signal at δ6.2 is assigned to the 5-proton H_c adjacent to the methyl group. and represents a downfield shift relative to spirodiene **9** of approximately 0.1δ.

The latter assignment is presumed incorrect because the methyl inductive effects are in opposite directions in **36** and **37** and not equivalent in magnitude (+0.1δ to -0.77δ). The previous assignments are presumed correct because the shifts of H_c are both upfield and of approximately equivalent magnitude (-0.31δ and -0.4δ). The final assignments of the olefinic protons in 4- and 5- methyl spirodienes **36** and **37** are made (Figure 4).

The complete spectrum of 4-methyl spirodiene **36** (Spectrum 3, Appendix A) demonstrates that the 4-methyl signal is observed at δ1.7. The 5-methyl spirodiene **37** (Spectrum 2, Appendix A) shows 5-methyl absorption at δ2.05. These characteristic chemical shifts will be of use later in the assignments of the five isomeric trimethylspirodienes, **42** - **46**.

The spectral effects of *cis* and *trans* dimethyl substitution of the cyclopropane ring are best characterized by observing the nmr spectra of *cis*- and *trans*-2,3-dimethylspiro[2.4]hepta-4.6-dienes **38** and **39**. The AA'BB' pattern of the olefinic region clearly shows (Spectra 4 and 5, Appendix A) *cis*- and *trans*-configuration on the cyclopropane ring, due to the loss of the plane of symmetry coincident with the plane of the cyclopropane ring, when the methyl groups are *cis* to one another.

The *trans*-dimethylspirodiene **39** is of higher symmetry than the *cis* compound, **38**. A C_2 symmetry rotational axis through the spiro atom of **39** exists relative to the reflection plane coincident with the plane of the three ring in unsubstituted **9**. There is no such symmetry element in the *cis* spirodiene **38**. The olefinic region of *trans*-**39** (spectrum 4, appendix A) is almost superimposible to the same region of spirodiene **9**, although somewhat compressed.

The olefinic signals of the *cis*-dimethylspirodiene **38** (Spectrum 5, Appendix A) shows a highly complex splitting pattern that, upon scale expansion (60Hz sweep), yields four separate signals each integrating for one proton. The additional splitting is consistent with the loss of symmetry due to *cis* substitution of the cyclopropane ring.

The methyl absorption in *trans*-dimethylspirodiene **39** is a doublet (J = 5.4Hz) at δ1.27 to δ1.45. The methyl signal in *cis*-dimethylspirodiene **38** is also a doublet (J=6Hz) but with a larger coupling constant and with some additional line structure not seen in the *trans* compound **39**. There is no appreciable chemical shift differences between the methyl groups in **38** and **39**.

The characterization of *cis*-2,3-dimethylspiro[2.4]hepta-4,6-diene **38** permits verification of the stereoselectivity of the carbene synthesis[36] used in the preparation of the trimethylspirodienes **42-46**. The reaction of diazocyclopentadiene **48** and *cis*-2-butene was accomplished[34] in 15% overall yield. The yield of *cis*-dimethylspirodiene **38** relative to *trans* **39** was 19:1, consistent with stereoselectivity of the reaction discussed above (Results and Discussion; Synthesis).

The isolated substituent effects can be put together in conjunction with experimental evidence to characterize the trimethyl spirodienes **42-46**. Two of the five isomers were prepared earlier by the dibromide route (see above). Two isomers are isolated from the reaction mixture in low yield. The spectral data indicate that one is a 5-methyl isomer based on methyl absorption at δ2.05 (Spectrum 6, Appendix A). The olefinic signals are almost superimposible with 5-methylspirodiene **37**, although quite compressed. The dimethyl absorption compares closely with the slightly lower order coupling demonstrated in *trans*-dimethyl spirodiene **39** above.

The other trimethyl isomer from the reaction is assigned as *trans*-2,3,4-trimethyl spiro[2.4]hepta-4,6-diene (45; Spectrum 7. Appendix A). The olefinic signal is almost superimposible with the olefinic signal from the 4-methylspirodiene **36**. The dimethyl signal shows the lower order coupling of *trans* configuration of methyl substituion on the three ring. However, the 4-methyl signal is observed about 0.2δ downfield from predicted by comparison to 4-methylspirodiene **36**, but is considerably upfield from the 2.05δ characteristic of 5-methyl substitution. This anomaly may in part be explained by interaction of the 4-methyl group with the cyclopropane methyl group directed towards it. The other cyclopropane methyl group is directed away from the 4-methyl substituent.

These assignments cannot be made absolutely without citing further experimental evidence. The experimental evidence obtained in this research *via* the carbene synthesis is of *cis*-2,3,4- and *cis*-2,3,5-trimethyl isomers, in conjunction with the proven stereoselectivity for the *cis* configuration of that synthesis is reasonably compelling. Three previously unknown trimethyl spirodienes were isolated from the carbene synthesis reaction mixture along with 20% spirodiene yield of *trans*-2,3,4- and *trans*-2,3,5-trimethylspirodienes **45** and **46**. The two isomers are superimposible with those obtained in the dibromide synthesis of trimethyl spirodienes **45** and **46**. The carbene synthesis is known to be highly stereoselective by retaining the geometry of the reagent olefin. (See above, Results and Discussion: Synthesis) Although 20% of the total spirodiene yield was *trans*-, the assumption of the *cis* configuration for the remaining three previously unknown trimethyl spirodienes is quite reasonable, since the reagent olefin is *cis*-2-butene. One *cis* trimethyl isomer is not found in the carbene synthesis route and it is suggested that this is *cis*-2,3,7-trimethylspiro[2.4]hepta-4,6-diene. The proximity through space of the three methyl groups

causes adjacent hydrogen atoms to be an approximate distance of one angstrom unit from each other. This hydrogen-hydrogen compression may well preclude formation of the molecule.

Analysis of the nmr data using the above derived criteria for 5-methyl substitution of 5-methyl absorption at ca. 2.0δ and 4-methyl at ca. 1.7δ show that three of the five isomers are 5-methyl (Spectra 6,9,10; Appendix A). The remaining two isomers are 4-methyl substituted. Two isomers (**45** and **46**) are previously known from the dibromide synthesis and demonstrate less line structure in the signals for cyclopropane methyl at δ1.3 than the other three isomers.

The three previously unknown trimethyl spirodienes, **42,43,44**, are *cis*-2,3,4-trimethyl spirodiene **42** (a 4-methyl isomer) and the two 5-methyl isomers. The nmr spectrum of **42** shows 4-methyl substitution absorption at δ1.7. higher order splitting commensurate with *cis*-2.3 dimethyl substitution of the three ring and olefinic signals almost superimposible with 4-methyl spirodiene **36** (Spectrum 3, Appendix A).

The two remaining isomers are 5-methyl substituted based on the five ring methyl signals at δ2.05 - δ2.1 (Spectra 9,10; Appendix A). The 2,3 dimethyl signals of both spectra have greater line structure than **42, 45** and **46** and are characteristic of *cis*-2,3-dimethyl substitution of the cycloprane ring as derived above.

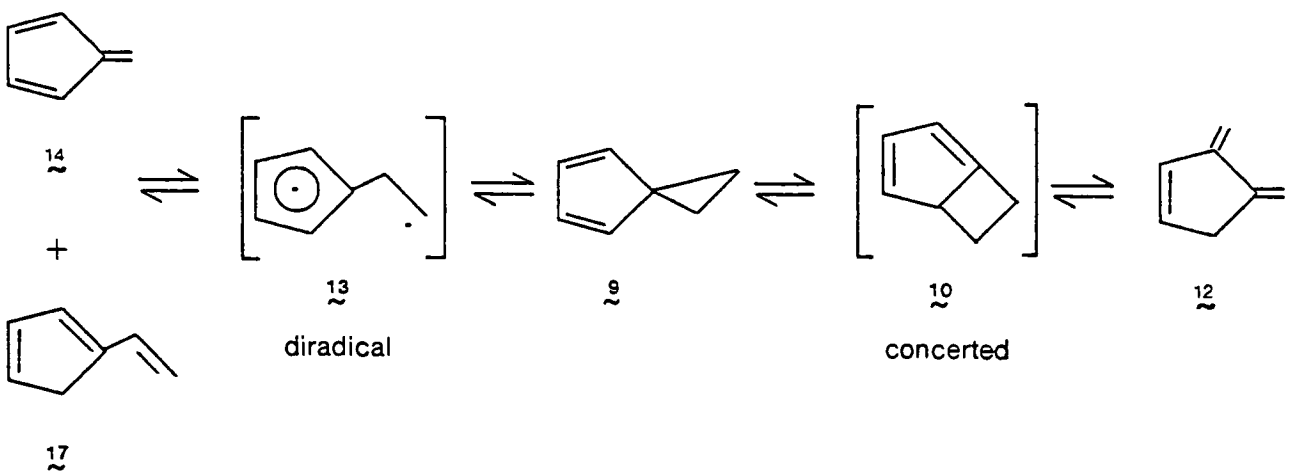
The assignment of *syn* vs *anti* configuration of the **5**-methyl substituent is not readily derived from nmr data alone. Although the olefinic signals of the two isomers are clearly different. the relationship to previously characterized compounds is not apparent. Each olefinic region (Spectra 9 and 10; Appendix A) has one-half the characteristic mirror symmetry present in other spirodienes: one is a downfield (5-position) proton (Spectrum 9, Appendix A); the other is an upfield (4-position) proton (Spectrum 10, Appendix A). The other proton in both compounds with the other half of the mirror symmetrical pattern is overlapped by the H_c, the 4-proton adjacent to the methyl group.

Nevertheless, one *cis*-trimethyl spirodiene, **42**, is confidently characterized and is an adequate beginning for this research involving the thermal rearrangement of spiro[2.4]hepta-4,6-diene **9**.

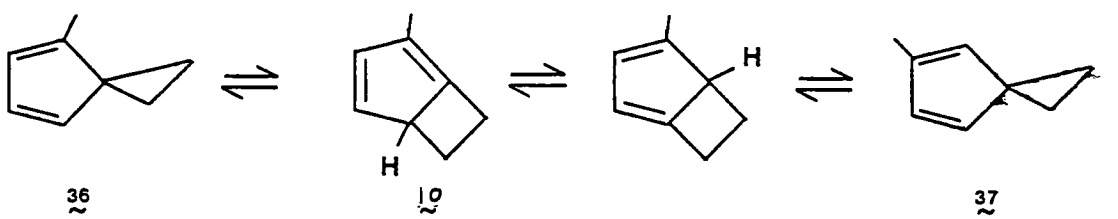
IV. Thermal Rearrangements

Previous studies of the thermal rearrangement of spiro[2.4]hepta-4,6-diene, **9**, are vague in determining whether the 1,5- alkyl migrations proceed *via* a diradical or concerted mechanism. The work of Krekels, Dane, deHaan and Kloosterziel[15,16] implies a delicate energy balance between the pathways (Scheme 17) with the proposed diradical mechanism

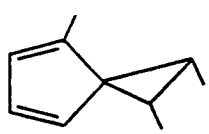
Scheme 17



fulvene products. **14** and **17** favored with increasing reaction temperatures. Evidence for the intermediacy of the bicyclo[3.2.0]heptadiene intermediate and the activation parameters for the thermal rearrangement of the 4-methyl-spiro[2.4]hepta-4,6-diene, **36**, to the 5-methyl spirodiene were obtained by D. S. Youngs[25,34]. The exact mechanism of formation of the bicyclo[3.2.0]heptadiene intermediate proposed as involved in the cyclopropane ring walk around the periphery of the cyclopentadiene ring system is unknown.

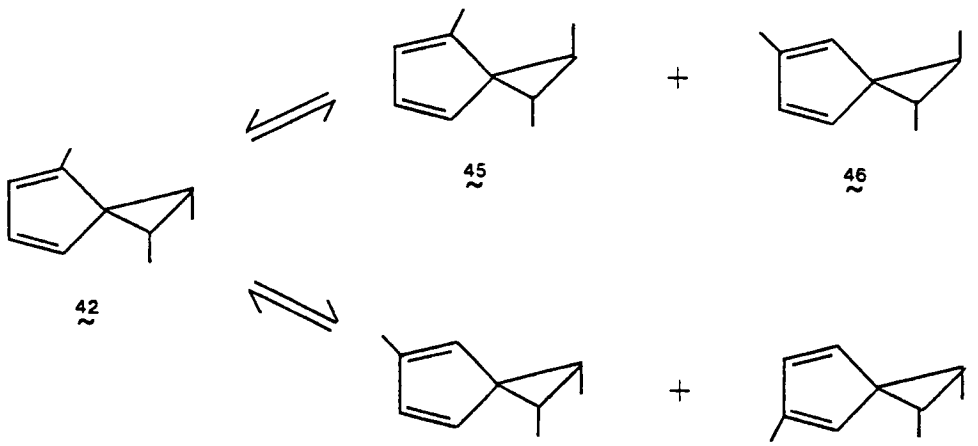


The synthesis and characterization of *cis*-2,3,7-trimethylspiro[2.4]hepta-4,6-diene (see Results and Discussion, above) provides a suitable compound for the detection of diradical intermediacy involved in the formation of the analogous trimethyl bicycloheptadiene



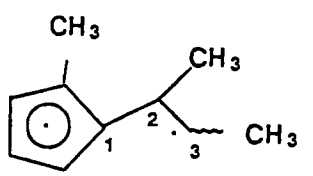
42

intermediate. The stereochemical *cis* dimethyl label of the three membered ring allows detection of homolytic cleavage of the C_1 - C_3 bond resulting in stereochemical scrambling of the *cis* dimethyl label. The methyl substituent of the five membered ring provides a label for detection of cyclopropane walk which may proceed through the bicyclo intermediate *via* a diradical or concerted process. Comparison of the relative rates of *cis* to *trans* isomerization and 4 - to 5- methyl migration are necessary to determine involvement of the diradical component of the mechanism.



42 **45** **46** **43 & 44**

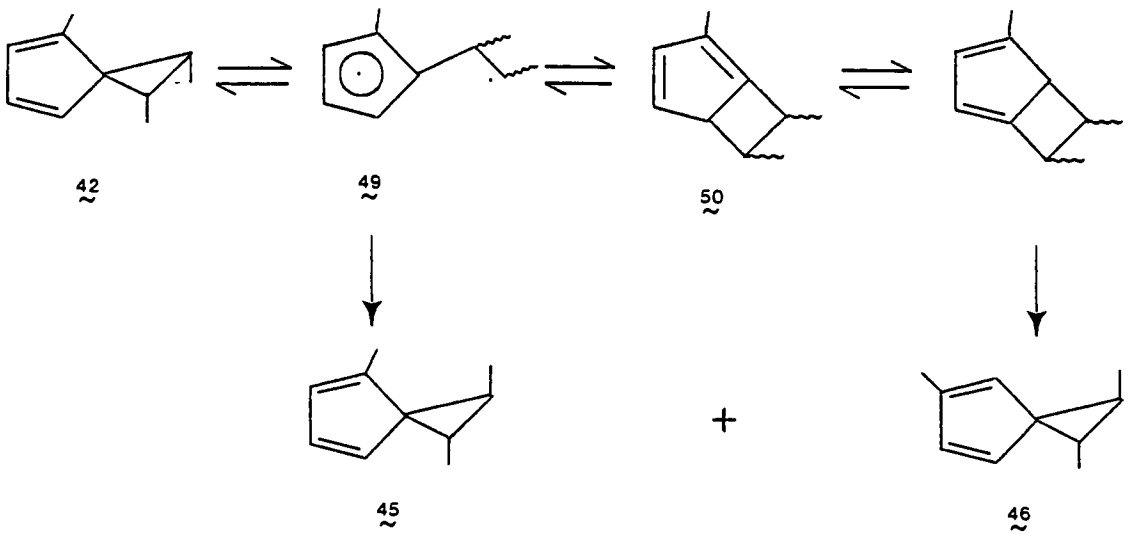
The involvement of a diradical intermediate, **49**, is assumed if a loss of stereochemical integrity of the *cis*-dimethyl label is observed. Rotation about the C_2 - C_3, and bond axes is permitted in the intermediate and results in formation of the more stable *trans* dimethyl



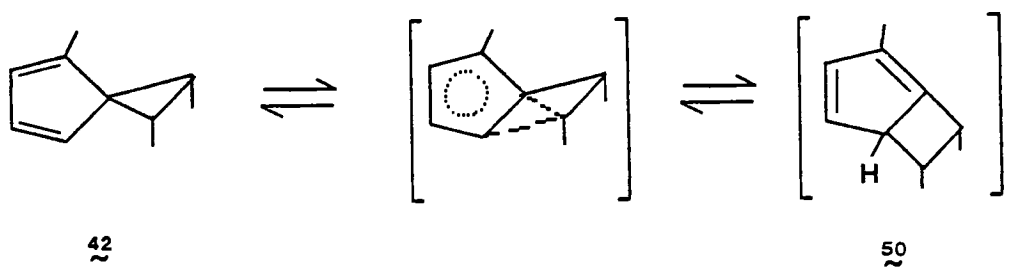
49

configuration upon subsequent ring closure to the spiro[2.4]diene ring system. If the diradical is also involved in the proposed cyclopropane walk bicyclo heptadiene intermediate, **50**, the *trans* dimethyl spirodienes **45** and **46** will be observed (Scheme 18).

Scheme 18

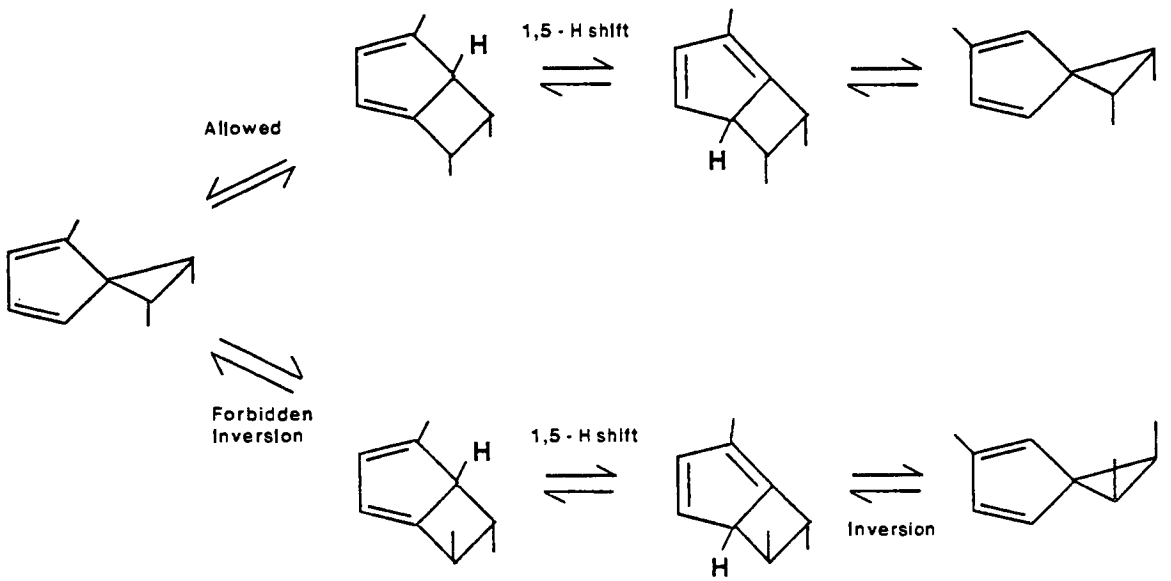


In either the concerted allowed or forbidden pathways (Scheme 19) no such rotation is permitted since at no time in the rearrangement is a bond completely broken. A relatively facile 1,5 hydrogen shift in the bicyclo trimethyl intermediate 50 followed by rearrangement to the spirodiene structure yields net 1,5 - alkyl migration with retention of stereochemistry.



The concerted allowed pathway proceeds by retention of configuration of the migrating carbon whereas the concerted forbidden pathway requires inversion of the migrating carbon atom. However, formation of the bicyclo intermediate 50 and subsequent formation of the trimethyl spirodiene is a dual alkyl migration resulting in overall retention of stereochemistry.

Scheme 19

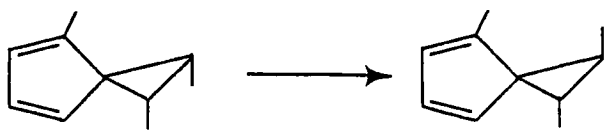


Therefore, concertedness is only potentially detectable. Differentiation between the concerted-allowed as opposed to concerted-forbidden is not possible by the present research. Although the forbidden pathway may proceed in preference to the diradical if the geometric constraints of the system override the electronic factors which favor the concerted allowed, it is felt that the geometric factors favor the concerted allowed. Retention of the *cis*- dimethyl configuration of the three membered ring is considered as probable evidence of a concerted-allowed pathway rather than progress of concerted forbidden in competition with diradical intermediacy.

The synthesis, isolation and characterization of *cis*-2,3,4-trimethylspiro[2.4]hepta-4,6-diene. **42**, resulted in a total yield of 0.15ml of 95% pure material as determined by analytical gas chromatography (see Experimental, above). The major impurity was the 4-*trans*-trimethylspirodiene, **45**. The thermal rearrangement was carried out in Carius tubes prepared by adding a mixture of **42** and n-butylbenzene and degassing the tubes at liquid nitrogen temperatures with three freeze thaw cycles and flame sealing the tubes under vacuum. A measured quantity of n-butyl benzene internal standard was added to determine decomposition rate. The Carius tubes were placed in a gas chromatograph column oven equilibrated at 220°C for the specific periods required for the rearrangement. Analysis of the product mixture was performed by opening the tubes to atmosphere followed by immediate addition of 0.06 ml pentane diluent and sealing of the tube with a septum. Analysis of the product mixture was carried out by analytical gas chromatography (see Experimental Section).

The rearrangement has approximately first order in disappearance of **42** as determined by concentration loss relative to n-butylbenzene internal standard (Figure 5, page 45). The

initial rapid loss of the *cis*-2,3,7-trimethylspirodiene **42** coincided with an approximately equal rapid appearance of the *trans*-4-trimethylspirodiene, **45**.

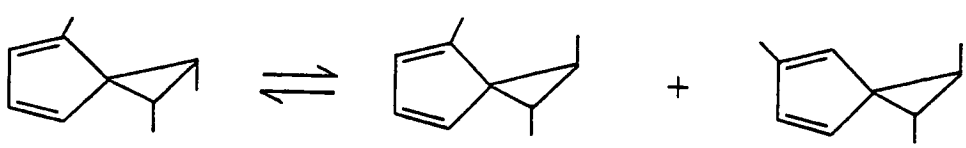


42 **45**

The *trans*-5-trimethylspirodiene **46** appeared at a much slower rate. The two rearrangements that proceeded to fifty and seventy hours contained approximately equal amounts of all three isomers and demonstrated considerable loss of spirodienes to decomposition. Decomposition up to twenty hours was five per cent or less. At pyrolysis times greater than twenty hours, decomposition increased to as high as eighty per cent in one sample.

The progress of the reactions is graphically presented in Figure 5, page 45, and shows the realtive concentration loss of **42** in comparison to the appearance of **45** and **46**, corrected for decomposition losses.

The significant observations of the thermal rearrangement reactions are the rapid initial disappearance of *cis* trimethyl spirodiene **42**; the rapid appearance of 4-*trans*-trimethyl spirodiene **45** and the perceptibly slower appearance of the 5-*trans* trimethyl spirodiene **46**. Also significant are the approximately equal concentrations of these three isomers in the fifty and seventy hour reaction mixtures. Further, no isomers were detected with both 5-methyl substitution of the five membered ring and *cis*-2,3-dimethyl substitution of the three member ring.



42 **45** **46**

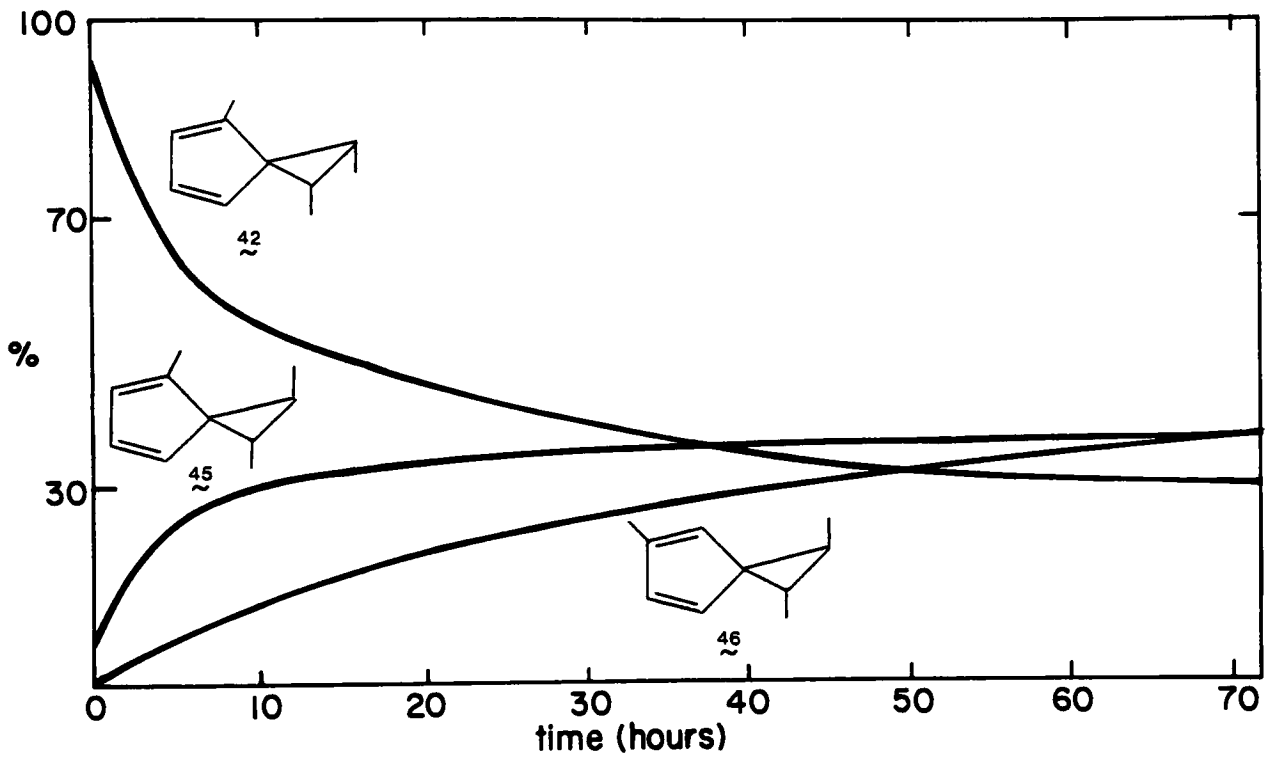
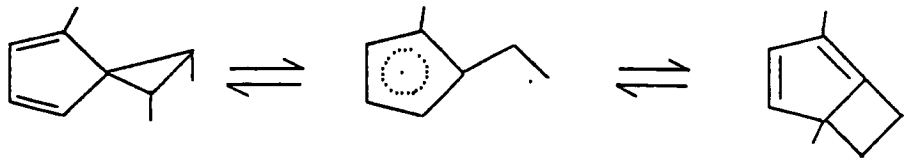


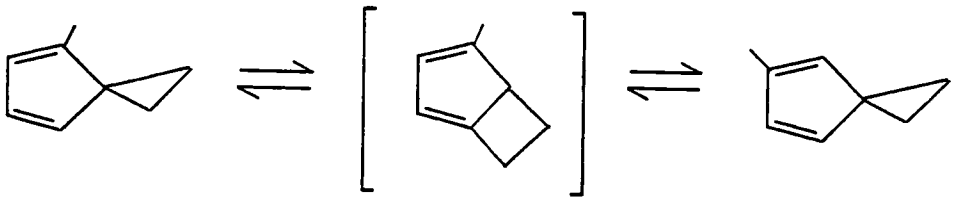
Figure 5. Per Cent Relative Concentration Spirodienes 42, 45 and 46 in Thermal Rearrangement Mixtures

The initial rapid rates of disappearance of the *cis*-trimethyl spirodiene 42 and appearance of the 4-*trans* isomer correlate well with a diradical intermediary to the bicyclo[3.2.0] intermediate 50 (see above). Previous studies by Youngs[25] which show a slightly positive



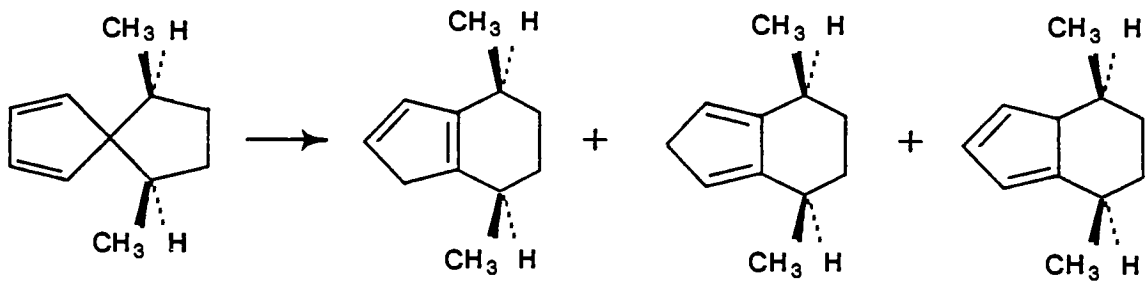
42 49 50

entropy of activation in the 4- to 5- methyl isomerization are also in support of a less organized transition state to the corresponding intermediate. The rearrangements of spirodiene 9 carried out by Kloosterziel[15,16] et al demonstrated a considerable diradical



45 46

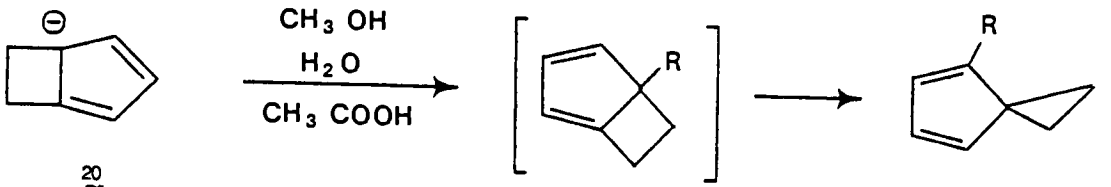
component favored by increasing temperature of the flow pyrolysis reactor. The parameters selected for thermal rearrangement in this research favor a concerted pathway the most. Their work demonstrated increasing diradical character with increasing temperature through the range of 345°C to 400°C. The thermal rearrangements in this research were carried out in a static system 220°C. The thermal rearrangements of less strained spirocyclopentadienes carried out in a micro flow pyrolysis reactor in the temperature range of 230°C to 280°C were shown to be completely stereospecific by Boersma, et al[20].



21a 22a 23a 24a

The conclusion that the reactions proceeded totally by the concerted pathway were based on the stereoselectivity of the reactions as well as the first order reaction kinetics. The final products in these reactions are analogous to the proposed bicyclo intermediates for the cyclopropane ring walk in the spiro[2.4]hepta-4,6-dienes, 10 and 50 (see above), but are not as highly ring strained and consequently are stable products.

The extent of ring strain influence was further demonstrated by the work of Oda and Breslow[19] in the formation of the highly reactive anion 10 which presumably is protonated

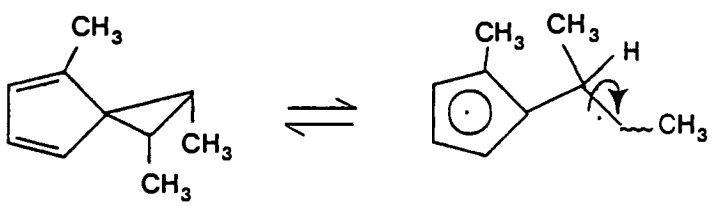


20 10 9

by various reagents to the bicyclo[3.2.0] intermediate but led to the spiro[2.4]hepta-4,6-diene 9 as the only distillable product.

Despite the comparatively mild temperature of 220°C used in this research to favor the concerted pathway, the initial rapid appearance of the 4-*trans* trimethyl spirodiene 45 is not obtained by a concerted process.

The loss of *cis* configuration of the three ring requires only opening of the C_1-C_2 bond to the diradical intermediate. Rotation rates of both the C_1-$C_2$and C_2 - C_3 bonds are competitive enough with the reverse three ring closure reaction. Formation of the

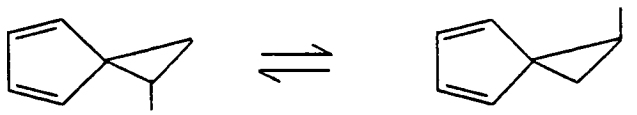


42 49

[3.2.0]bicyclo intermediate is not required in this step, but only in the 5-*trans* trimethyl spirodiene 46 which forms at a much slower rate in the thermolysates. The slower rate is consistent with the additional constraints of formation of this required, highly strained intermediate and a subsequent reaction sequence of a sigmatropic [1,5] hydrogen shift in that intermediate. It is not possible however, to exclude the operation of a concerted

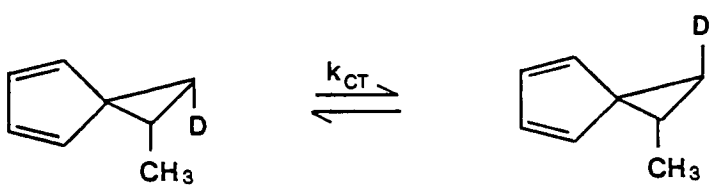
pathway leading to the 5-*trans* trimethyl spirodiene **46** in competition with the diradical pathway.

Given the apparent delicate energy balance between the two mechanisms it is reasonable to assume that any factors that would stabilize diradical intermediacy, such as alkyl substitution, in a 1,5 sigmatropic shift would lead to a comparatively slower concerted process that could not be visualized at all by this research. Gilbert and Bladwin[41] recently presented evidence to support that premise by synthesizing and pyrolyzing some novel spirodienes. The pyrolysis of the (+)-2-methylspiro[2.4]hepta-4,6-diene **51** led to an equilibrium mixture of starting material **51** and its enantiomer, (-)-2-methylspiro[2.4]hepta-4,6-diene, **52** at a rate of 7.3 ±0.4 x 10^{-5} sec^{-1} at 221°C. The similar pyrolyses



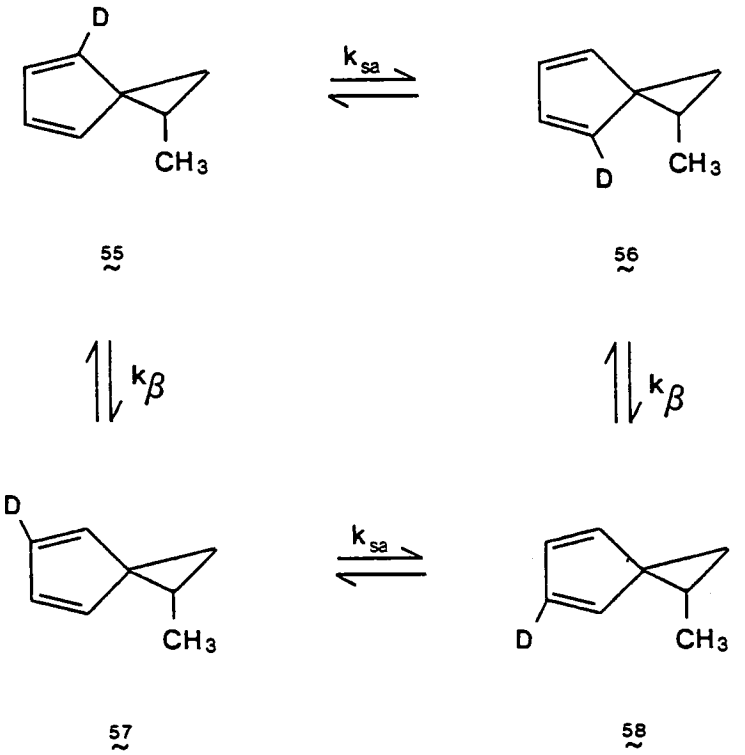
51 **52**

Z-2-methyl-3-deuterio-spiro[2.4]hepta-4,6-diene, **53**, led to an equilibrium mixture of starting *cis* spirodiene **53** and its *trans* analog, E-2-methyl-3-deuteriospiro[2.4]hepta-4,6-diene, **54**, at a rate of 7.2±0.5 x $10^{-5}sec^{-1}$.



53 **54**

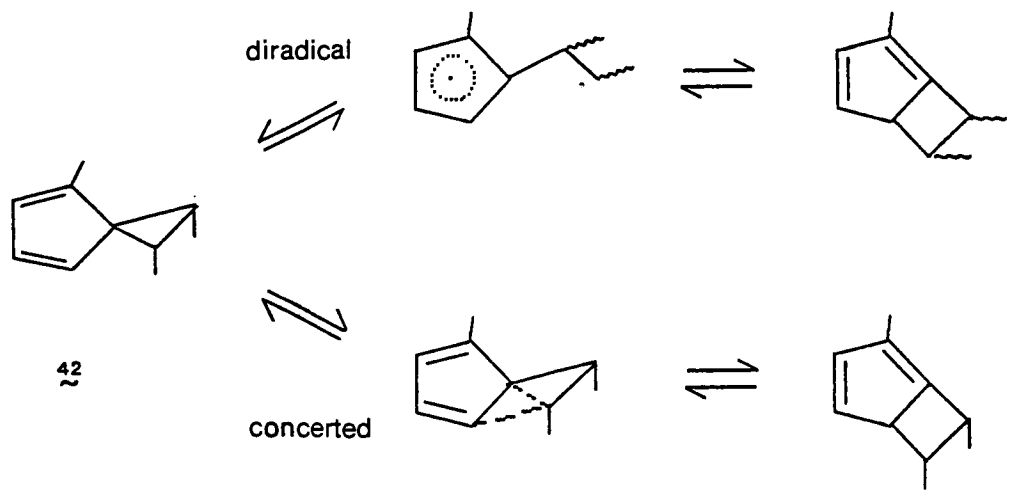
The geometrically and stereochemically labeled spirodiene, 2-methyl-4-deuteriospiro[2.4]hepta-4,6-diene, **55** led to a mixture of itself and three other isomers, 2-methyl-7-deuterio-(**56**), 2-methyl-5-deuterio-(**57**) and 2-methyl-6-deuterio- (**58**) spiro[2.4]hepta-4,6-dienes.



55 56 57 58

The measured rate of *syn-anti* (k_{sa}) stereochemical reorganization is 6.1±0.6 x $10^{-5}sec^{-1}$ as opposed to a significantly slower reorganization rate (k_{β})equal to 0.31 ± 0.04 x $10^{-5}sec^{-1}$.

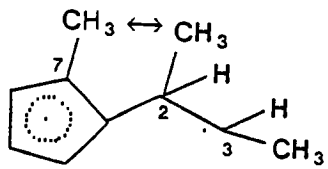
Although precise rate measurements are not available from the limited data obtained in this research, the results are in good agreement with those of Gilbert and Baldwin.[41] The first process to occur is loss of stereochemical organization of the three ring followed by a much slower 4-methyl to 5-methyl structural reorganization. These data are consistent with a diradical intermediate involved in the *cis* - to *trans* - rearrangement and either a concerted or diradical process leading to the bicyclo[3.2.0] intermediate required for structural reorganization.



42

Although firm evidence for a concerted pathway in less severely strained spirodienes (Boersma, et al - see above) exists it is not possible to prove with this data the operation of such a mechanism in the spiro[2.4]hepta-4,6-diene thermal rearrangement. However, it is clear that if the mechanism is operative, it is at a slower rate than the diradical process which leads to a loss of stereochemistry.

The presence of the starting material **42** in the equilibrium mixture is not conveniently explained and further work using other starting materials would be required to explain. One possible explanation is steric interaction of the methyl groups on C_1 and C_2 carbons in the diradical intermediate counteracting the less favorable *cis* orientation of the C_2 and C_3

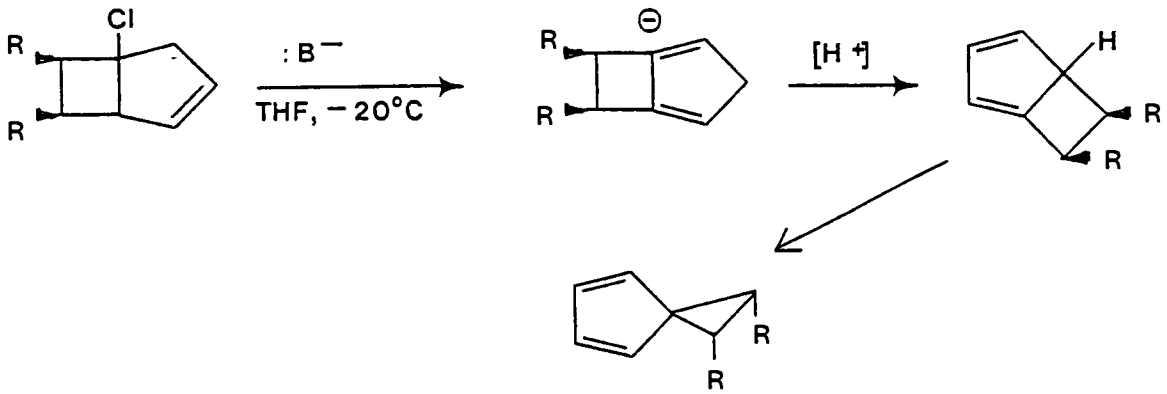


methyl groups. Whatever the cause, it is clear that the energetics are closely balanced. The fact that no *cis*-2,3,5-trimethylspirodienes (**43** or **44**) appeared at all in the product mixture is strong evidence only for comparatively slow operation of a concerted mechanism in comparison to the faster diradical mechanism. The lack of these products is not definitive proof that the concerted pathway is not operative.

The influence of increasing alkyl substitution of the cyclopentadiene ring system seems to favor the diradical pathway. As noted above, the unsubstituted spiro[2.4]hepta-4,6-diene **9** gave measurable concerted mechanism products even at substantially higher temperatures[15,16] (Scheme 9, page* Historical). The work of Gilbert and Baldwin with minimally substituted monomethyl spirodienes gave substantially reduced concerted pathway products (page*, Results and Discussion). The ability of increasing alkyl substitution to stabilize free radical intermediates is well known. The delicate energy balance between concerted and diradical processes in these reactions has been well demonstrated in this discussion. Any factors that even at very minor levels could tend to favor either process can, and seem to, have a significant influence on the outcome of the reaction(s).

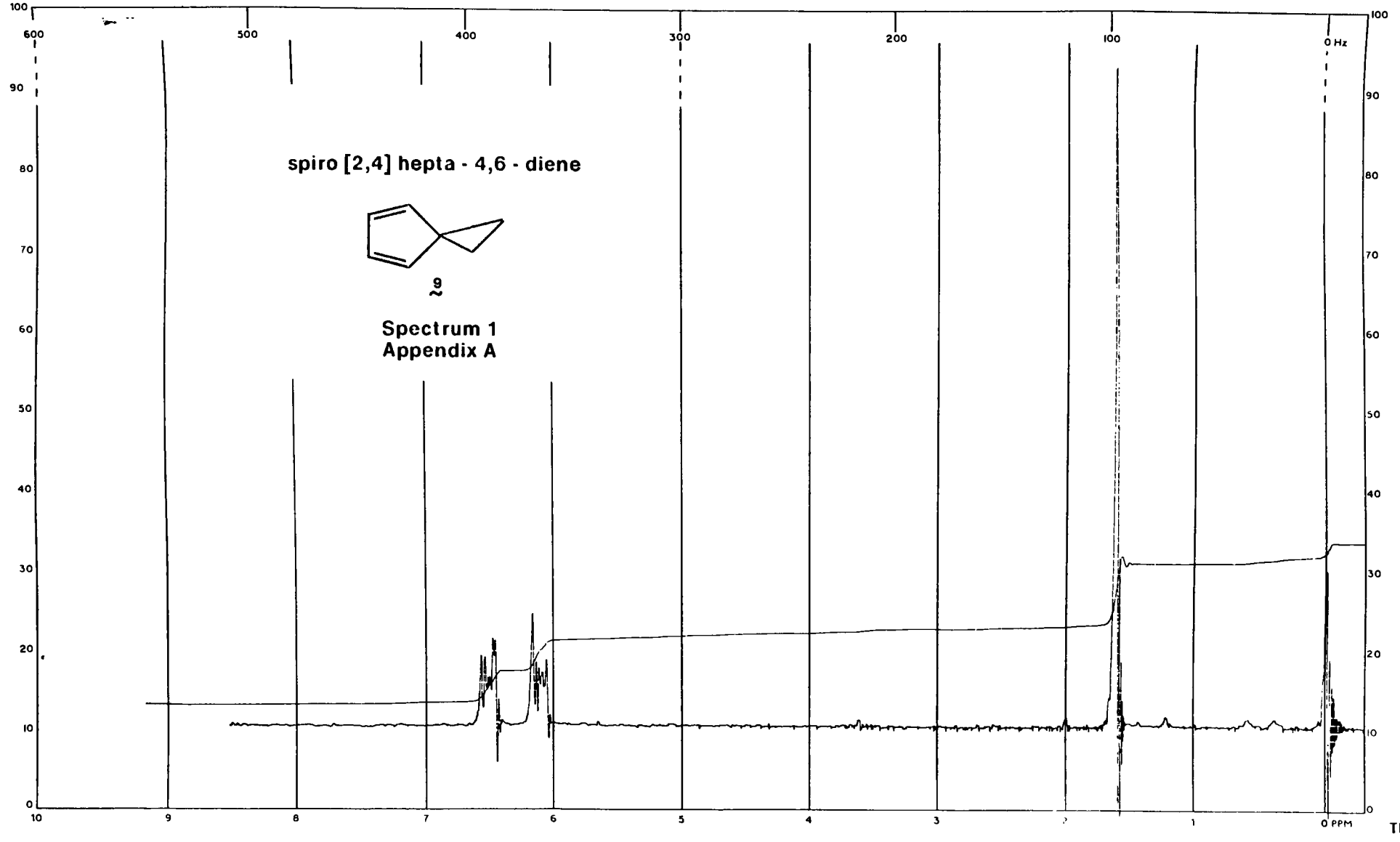
The observations of widely different competitive rates between concerted and diradical processes make certain observation of a concerted pathway tenuous at best. Only one research project referred to has reasonably unambiguous proof of the existence of the [3.2.0]bicyclo intermediate **10** and its relationship to the more stable spiro[2.4]hepta-4,6-diene **9** (Oda and Breslow[19]). Proof of the existance of a concerted pathway in these reactions could possibly be derived by the synthesis of the analogous substituted chlorobicyclo[3.2.0]heptene which would be dehydrochlorinated and subsequently

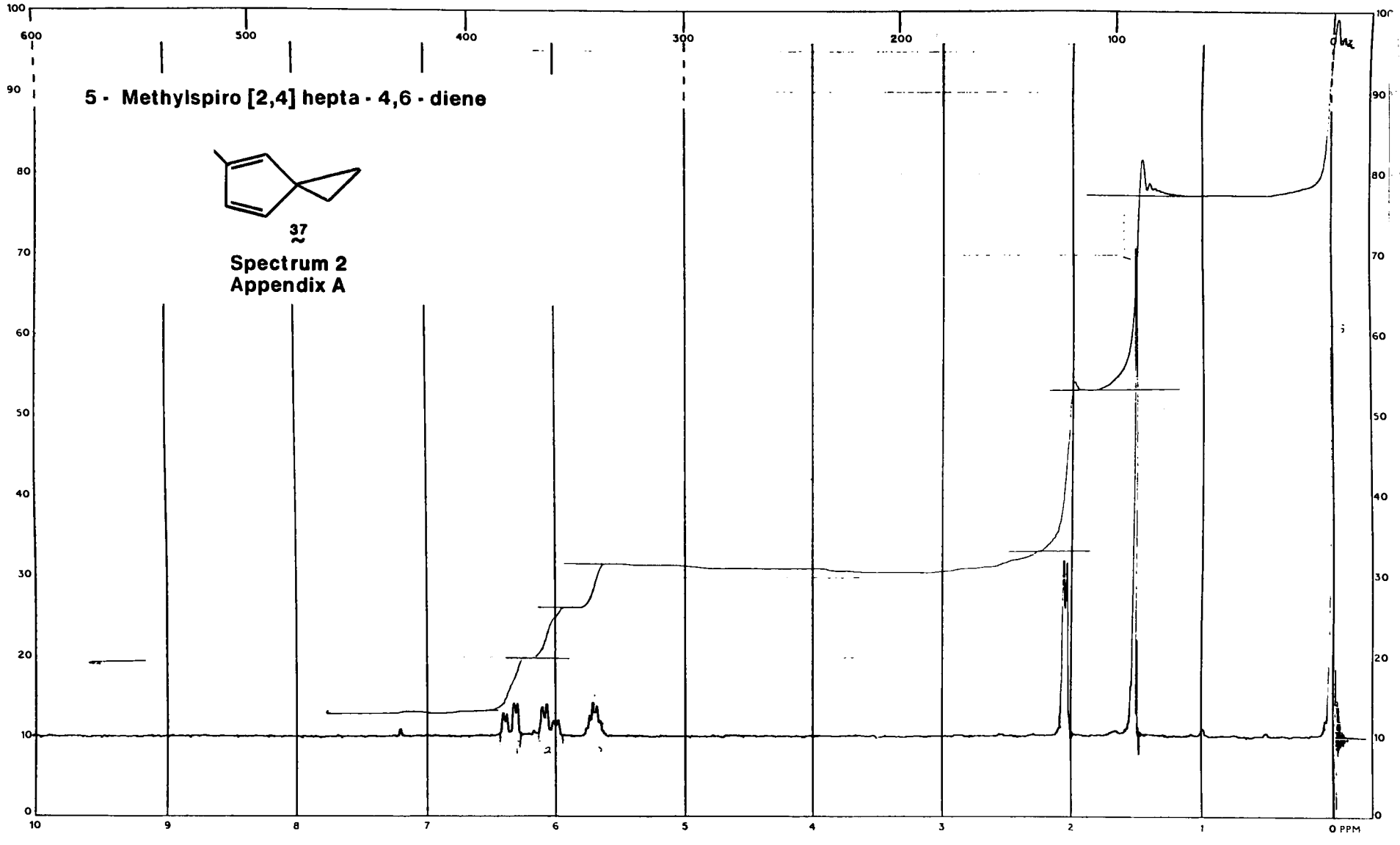
protonated to the bicyclo[3.2.0]heptadiene intermediate and ultimately the spiro[2.4]hepta-4,6-diene ring system.

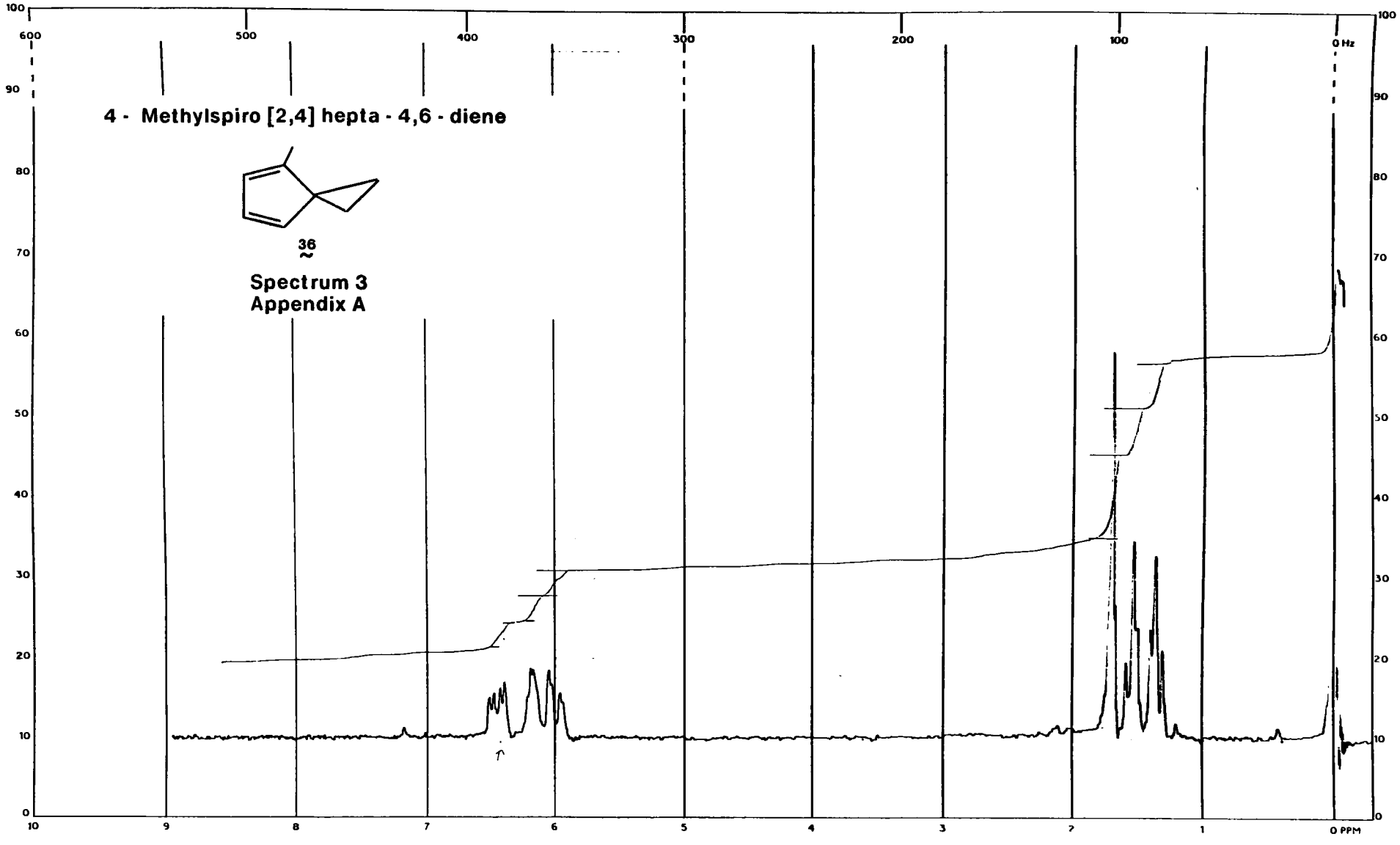


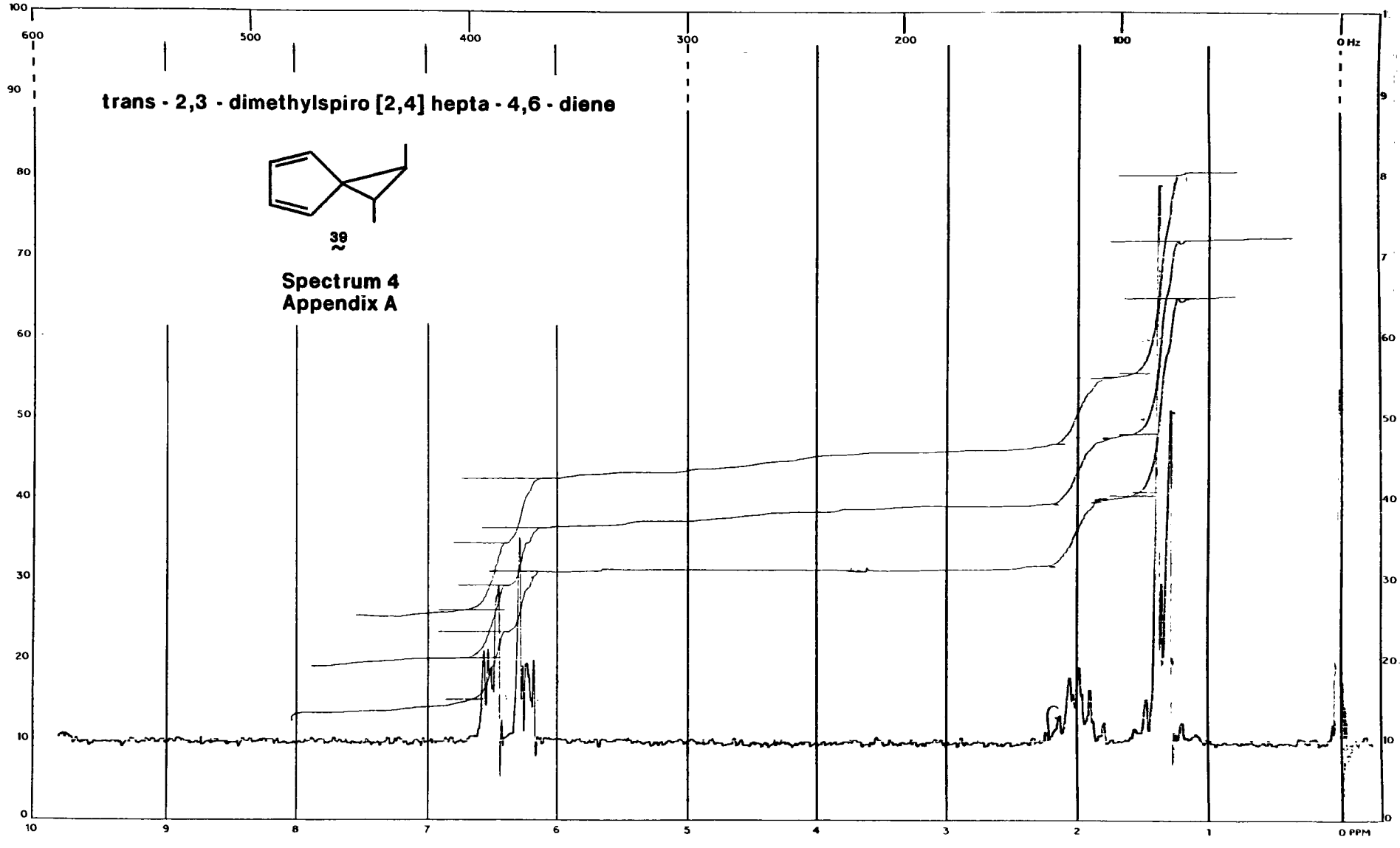
The nature of the alkyl substitution of the resultant spirodiene would be indicative of the stereoselectivity of the reaction. If *cis* labeled chloroheptene resulted in quantitative or nearly so, yields of *cis*-2,3-labeled spirodiene, this would be consistent with the operation of a concerted pathway. Any lack of stereoselectivity would be attributable to a diradical mechanism.

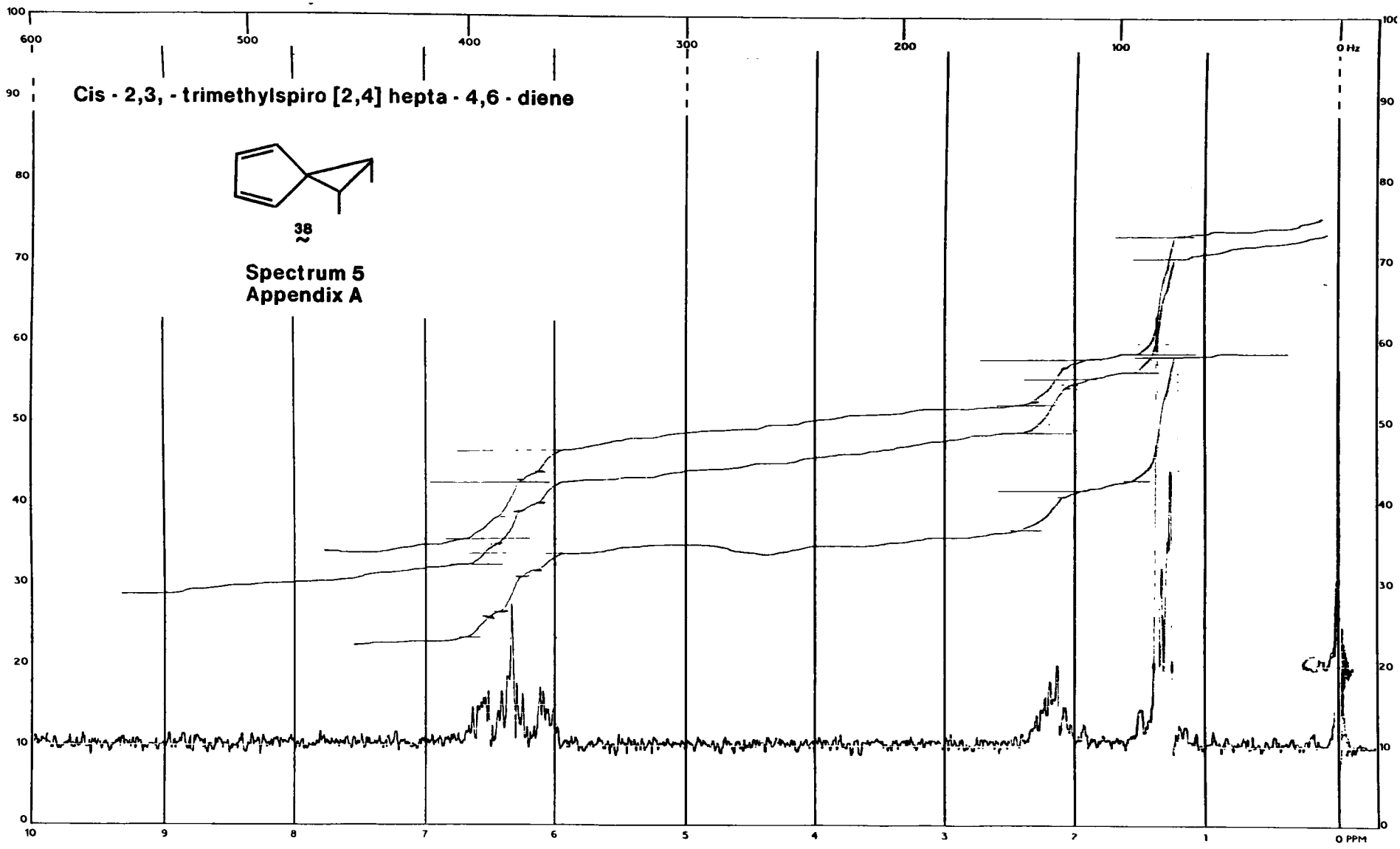
APPENDIX A

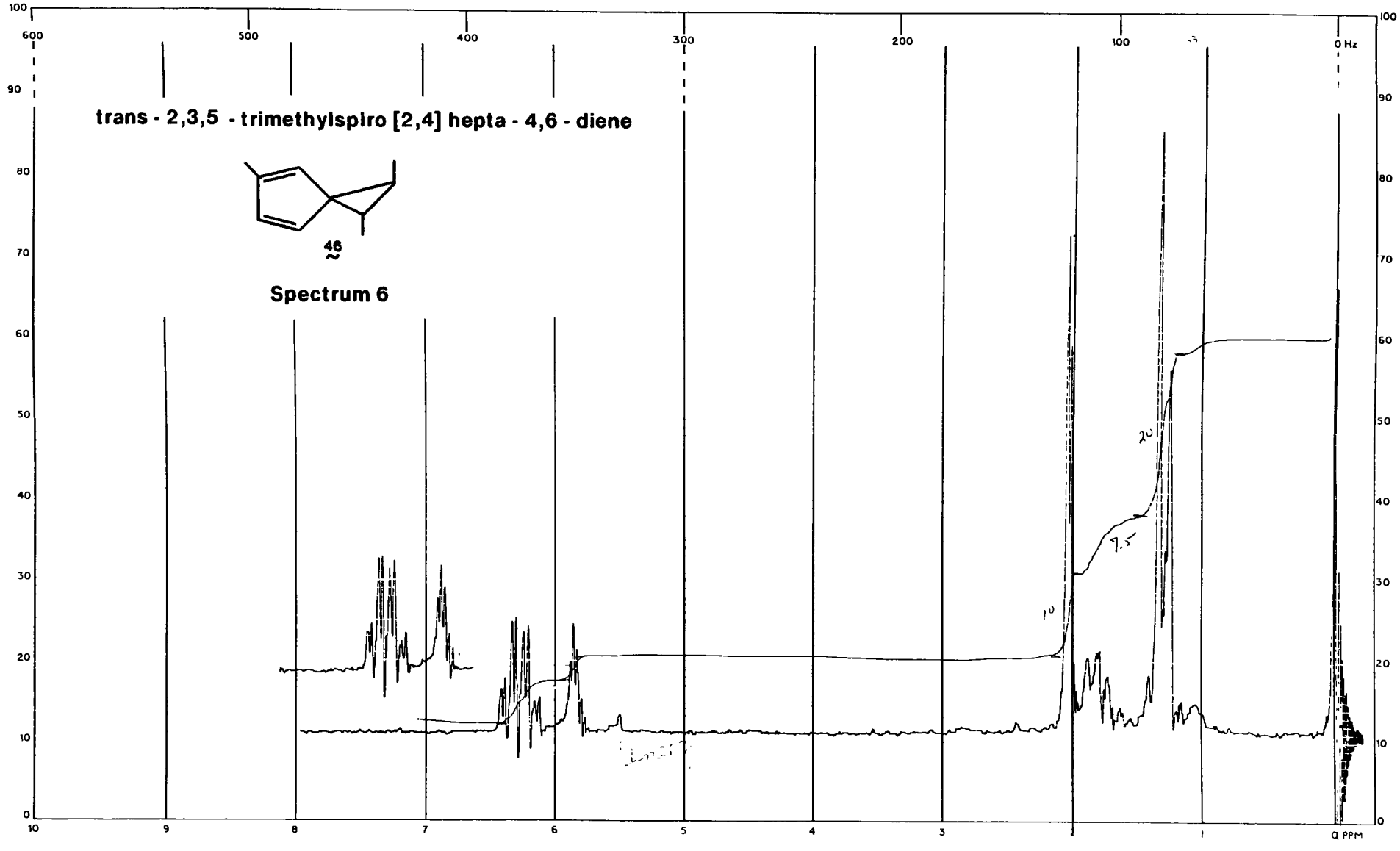

spiro [2,4] hepta - 4,6 - diene
9
Spectrum 1
Appendix A
600
500
400
300
200
100
0 Hz
0 PPM
TI

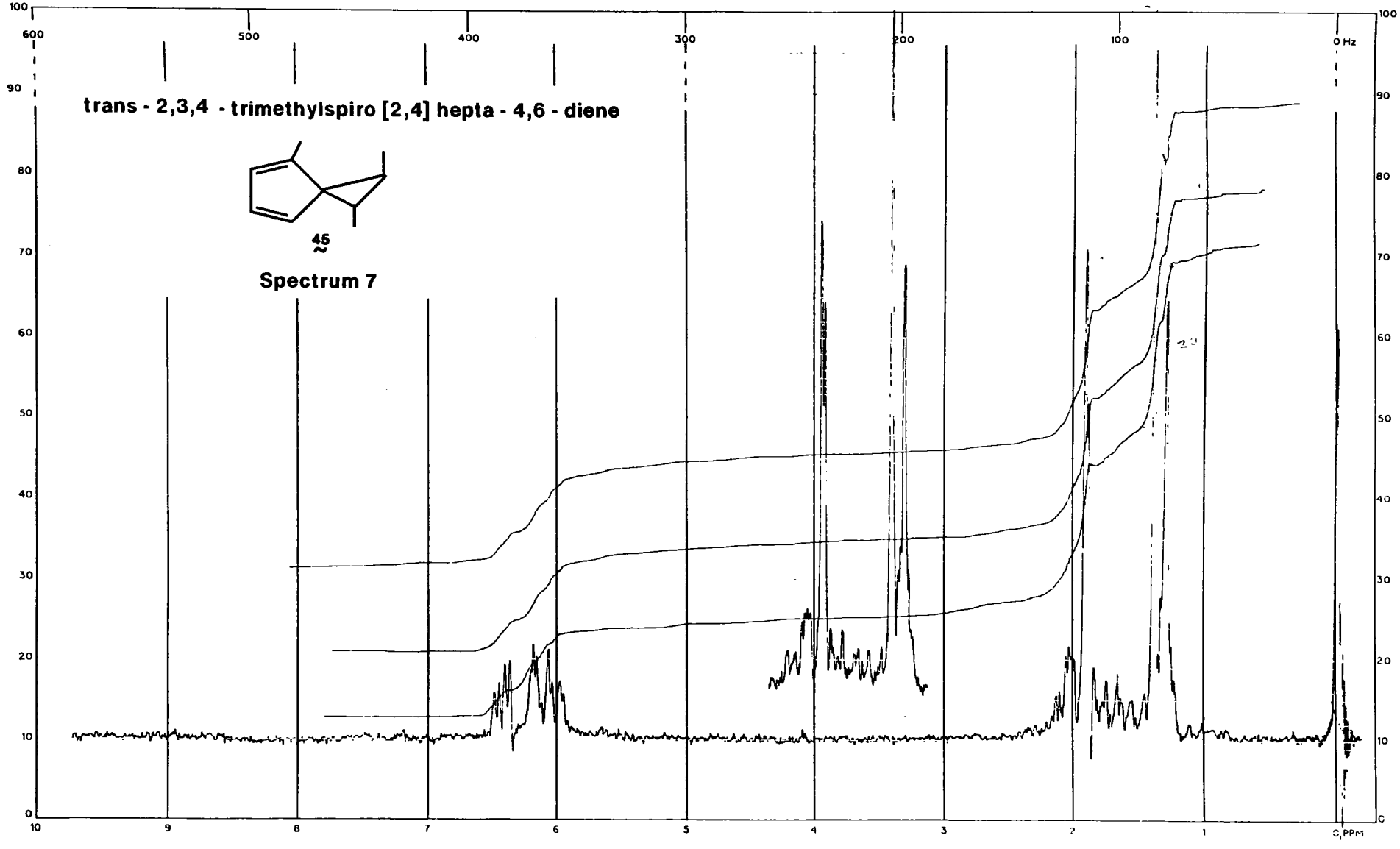

5 - Methylspiro [2,4] hepta - 4,6 - diene
37
Spectrum 2
Appendix A
600
500
400
300
200
100
0 Hz
100
90
80
70
60
50
40
30
20
10
0
10
9
8
7
6
5
4
3
2
1
0 PPM

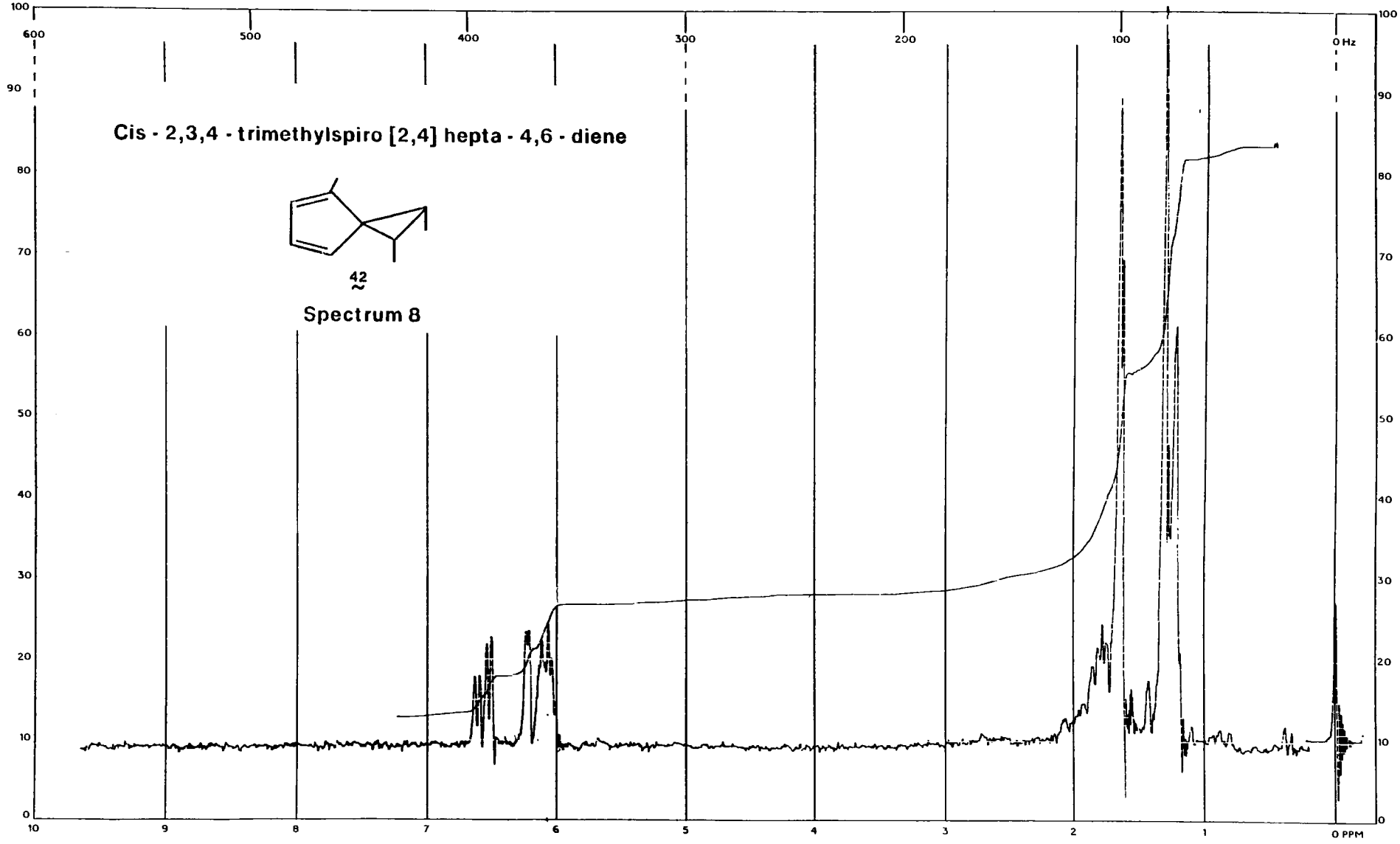

4 - Methylspiro [2,4] hepta - 4,6 - diene
36
Spectrum 3
Appendix A
600
500
400
300
200
100
0 Hz
10
9
8
7
6
5
4
3
2
1
0 PPM

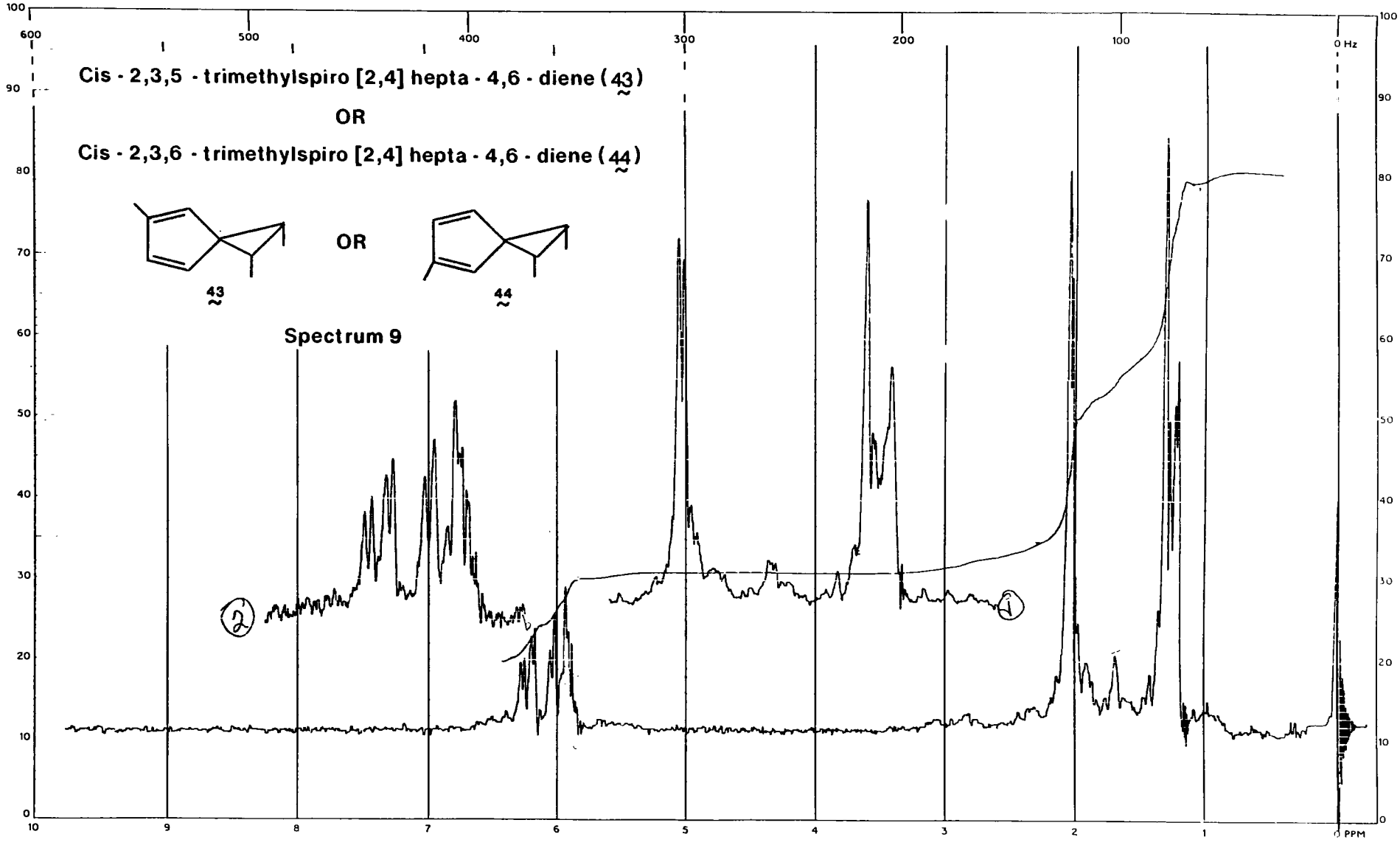

trans - 2,3 - dimethylspiro [2,4] hepta - 4,6 - diene
39
Spectrum 4
Appendix A
600
500
400
300
200
100
0 Hz
10
9
8
7
6
5
4
3
2
1
0 PPM

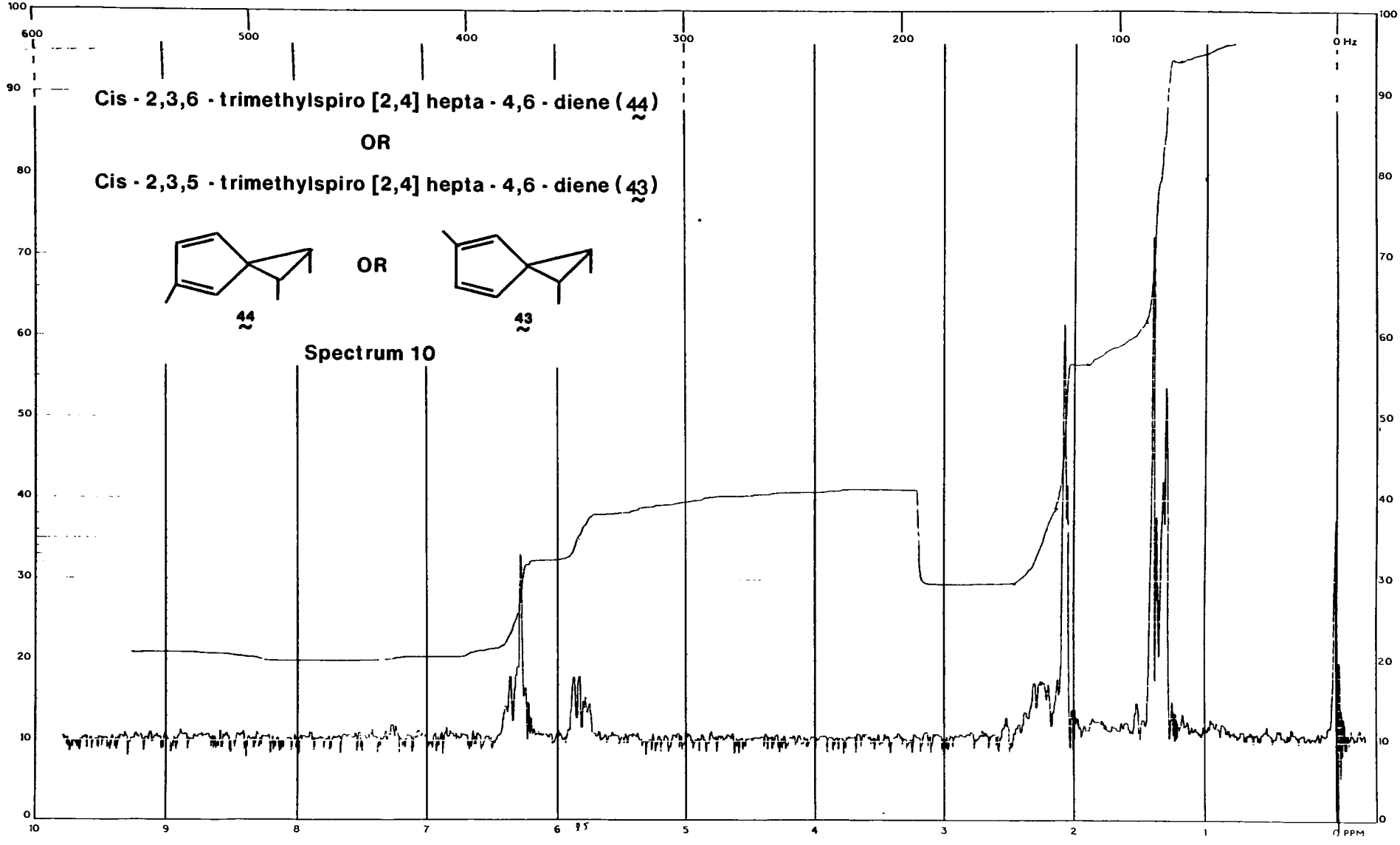

Cis - 2,3, - trimethylspiro [2,4] hepta - 4,6 - diene
38
Spectrum 5
Appendix A
600
500
400
300
200
100
0 Hz
0 PPM


trans - 2,3,5 - trimethylspiro [2,4] hepta - 4,6 - diene
46
Spectrum 6
600
500
400
300
200
100
0 Hz
10
9
8
7
6
5
4
3
2
1
0 PPM


trans - 2,3,4 - trimethylspiro [2,4] hepta - 4,6 - diene
45
Spectrum 7
600
500
400
300
200
100
0 Hz
10
9
8
7
6
5
4
3
2
1
0 PPM


Cis - 2,3,4 - trimethylspiro [2,4] hepta - 4,6 - diene
42
Spectrum 8
600
500
400
300
200
100
0 Hz
10
9
8
7
6
5
4
3
2
1
0 PPM


Cis - 2,3,5 - trimethylspiro [2,4] hepta - 4,6 - diene (43)
OR
Cis - 2,3,6 - trimethylspiro [2,4] hepta - 4,6 - diene (44)
OR
43
44
Spectrum 9
600
500
400
300
200
100
0 Hz
10
9
8
7
6
5
4
3
2
1
0 PPM


Cis - 2,3,6 - trimethylspiro [2,4] hepta - 4,6 - diene (44)
OR
Cis - 2,3,5 - trimethylspiro [2,4] hepta - 4,6 - diene (43)
OR
44
43
Spectrum 10
600
500
400
300
200
100
0 Hz
0 PPM

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